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SEMI-ANNUAL REPORT

on

Essential Oils,

Synthetic Perfumes, &c.

Published by

SCHIMMEL & Co.

(Fritzsche Brothers)

MILTITZ

near Leipzig

LONDON —:— NEW YORK

APRIL 1914

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General view of the works and employees' dwellings of the firm of Schimmel & Co., Miltitz near **Leipzig**
(the rose-fields in the foreground).

Photographed from the
Zeppelin air-ship "Sachsen".

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Contents.

Page

Introduction 5
Commercial notes and scientific information on essential oils 29
New essential oils 101
Chemical Preparations and Drugs 103
Notes on recent research work
General 119
Bibliography 120
Analytical 120
Physical 122
Pharmaco-physiological 124
Phyto-physiological 125
Chemical 126
Hydrocarbons 129
Alcohols 132
Aldehydes 136
Ketones 138
Phenols and Phenol-ethers 143
Acids 145
Nitrogenous Bodies 147

List of abbreviations.

d = specific gravity.
$d_{20°}$ = specific gravity at 20° (in references from our laboratories uniformly compared with water at 15°).
$d_{4°}^{20°}$ = specific gravity at 20°, compared with water at 4°.
$\alpha_{D20°}$ = optical rotation at 20°, in a 100 mm. tube.
$[\alpha]_D$ = specific rotation.
$n_{D20°}$ = index of refraction at 20°.
Sol. p. = solidifying point.
M. p. = melting point.
B. p. = boiling point.
n = normal.
acet. = acetylation.
Acid v. = acid value; ester v. = ester value; sap. v. = saponification value.
g. = gram; cc. cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

Miltitz near Leipzig, April 1914[1]).

The retrospect which it is our custom, in our April *Report,* to cast upon the past year, may on the present occasion again be characterized as, on the whole, a very gratifying one, and although the commercial result of the year 1913, considered from a purely financial standpoint, falls somewhat below that of 1912, the fact must be taken into account that the last-named year constituted a record, and that from the beginning it appeared to be out of the question, in view of the backward movement of the world's markets, that similar results would again be achieved. Further on in these introductory notes we shall have occasion to show that the chemical industry of Germany was one of those which suffered least by the downward turn of the markets, and we are fortunately able to affirm that the same thing applies to our own branch of industry. With few exceptions, our turnover in all the numerous selling-markets, and in the various industries in which our manufactures are used, has again made notable steps in advance; no new disturbances have to be registered in the international exchange of commodities, and it is only due to the downward course of prices in the principal articles of our trade (a tendency which was assuredly to be expected after the upward movements of the preceding year), that the net profits realized bore no proper proportion to the increase in the turnover.

During the greater part of the year 1913 the political situation of Europe continued to suffer directly from the effects of the Balkan war, the consequences of which might have been immeasurable but for the cautious and peace-loving attitude of the Great Powers. These threatening complications naturally alarmed trade and industry, and the warlike preparations of Russia and Austria, as well as the increase in the armies of Germany and France, were factors which provoked a feeling of nervousness in all countries of Europe, which were attended by restriction in the desire for new enterprises, and which impeded the profitable development of most branches of commerce. The Triple Alliance has again proved to be the sheet-anchor of peace. Compared with the grave political occurrences in Europe, the disorders in Mexico and the revolution in China, which reached their culminating point in the course of last year, recede altogether into the background. The civil war between North and South in China which preceded the Presidential election, concealed within itself the germ of complications into which Europe might easily have been drawn. This danger, too, has fortunately been overcome.

The restoration of composure in international politics during the closing months of the year has brought about that relaxation of tension in the money-market which we forecast in our last *Report,* and has consequently removed an impediment of which the far-reacting effects cannot be over-estimated. "Under the influence of the economic upward movement and the political apprehensions" (the Report of the Board of Directors of the *Deutsche Reichsbank* for 1913 begins), "the strain on the money-market

[1]) The introduction to the present Report, and the Commercial part, were written in the month of March.

continued during the first part of last year, with the result that until after the close of its first half the demands upon the Reichsbank were exceptionally severe. Not until July did these demands begin to show a notable contraction, in consequence of the decline in the upward movement in business, the diminution of Stock Exchange activity and the general return-flow of the money which had been hoarded up in the previous year owing to the fear of war. The condition of ease which returned to the German money-market after the autumn, and the steady improvement of the balance in the Reichsbank made it possible, on October 27, to reduce the bank-rate to $5^1/_2$ p.c., after which the Bank was able, contrary to custom and owing to the continuation of the favourable conditions, to declare a further reduction to 5 p.c. even before the close of the year, on December 12.

The improvement in the bank-balance was effected principally by the considerable increase in the holdings of gold. This increase, apart from the return of hoarded moneys and the enlarged issue of small bank-notes, is to be ascribed to the favourable turn taken by the commercial balance of Germany, and to the heavy purchases of gold abroad connected therewith. On 23rd April the gold-reserve for the first time exceeded 1000 million marks, and on 22nd November it reached its highest point at 1255 million marks. At the close of the year the Bank's gold-reserve was 1170 million marks, or 393 million marks in excess of that at the end of 1912".

As might be expected, the favourable state of the money-market reduced all those pessimists to silence, who even at the beginning of the year declared an economic crisis to be unavoidable in the year 1914. Nobody will of course deny that after a series of economically propitious years a reaction must set in sooner or later, but all those who have followed the course of trade and traffic during the last few years with some amount of understanding will energetically dispute the assertion that just at the present time there is reason for looking upon the development of affairs in the year 1914 otherwise than in an attitude of quiet confidence. There is scarcely an industry in which there is an exceptionally large stock of finished manufactures, the greater cheapness of money promotes enterprise; throughout the world, as the result of good harvests which have been gathered in most countries overseas, an increase in the sale of German goods is to be expected, the quietness which has been restored in the Balkans is opening good prospects for business in those countries, as well as in Austria-Hungary and in Russia; and, finally, the economic importance of the reform in the United States Tariff is certain to manifest itself more clearly in the future than is now the case. All these are entirely encouraging facts and it would be contrary to common sense to form an unfavourable opinion of the future, merely because of the traces of a certain feeling of lassitude which have lately shown themselves in some branches of German industry. The reaction upon the economic life of Germany, of the new Army-taxes the effects of which it is of course impossible to gauge at present, should not, in our opinion, be over-estimated, for of this there can be no question that the national wealth of our people has increased at a marvellous rate during the last few years, and that it is therefore thoroughly equal to make the necessary sacrifices, which, moreover, will chiefly result in further gain to the industries of the country.

The general condition of business in our branch of industry gives no cause for fresh observations. The unfair business-practices of certain firms, who regard it as a matter of honour to serve their customers cheaply, it is true, but with adulterated wares, has often been a matter of complaint already. In spite of the revelations of our research-laboratory these practices are steadily going on, but from the replies

received from those of our friends who employ us regularly to control goods supplied to them, we gather with satisfaction that our efforts are attended by success in many directions. We again extend an invitation to our readers to avail themselves of the free services of our laboratory, and we will only remark in passing that we are about to enlarge our scientific department considerably by the addition of a new floor.

Our sales in Germany have moved within the limits of normal business-requirements, and we have been able to notice few signs of any reversal in the generally propitious condition of trade. The industries in which our manufactures are used have been apparently very busy, and although here and there some lack of enterprise was shown, trade in general may be described as normal and healthy. Naturally, the downward movements in the prices of our principal manufactures have not helped to stimulate sales, for of course most buyers take up an attitude of reserve, and only cover their most urgent needs.

The respective shares of the four principal commercial nations in the trade of the world have been as follows:—

GERMAN EMPIRE

Exports, value	10080,6 Mill. ℳ (comp. w. 1912 +1123,8)	
Imports „	10695,4 „ „ („ „ 1912 + 4,0)	
	20776,0 Mill. ℳ (comp. w. 1911 +1127,8).	

UNITED KINGDOM

Exports 525,46 Mill. £ (comp. w. 1912 +38,24)	or 10719,4 Mill. ℳ (comp. w. 1912 + 780,1)	
Imports 769,03 „ „ („ „ 1912 +24,39)	„ 15688,2 „ „ („ „ 1912 + 497,6)	
	26407,6 Mill. ℳ (comp. w. 1912 +1277,7).	

FRANCE

Exports 6875,40 Mill. *fcs.* (comp. w. 1912 +162,8)	or 5500,4 Mill. ℳ (comp. w. 1912 + 130,3)	
Imports 8508,30 „ „ („ „ 1912 +277,6)	„ 6806,7 „ „ („ „ 1912 + 222,1)	
	12307,1 Mill. ℳ (comp. w. 1912 + 352,4).	

UNITED STATES

Exports 2484,31 Mill. $ (comp. w. 1912 +85,09)	or 10434,1 Mill. ℳ (comp. w. 1912 + 357,4)	
Imports 1792,18 „ „ („ „ 1912 −25,89)	„ 7527,2 „ „ („ „ 1912 − 108,7)	
	17961,3 Mill. ℳ (comp. w. 1912 + 248,7).	

In respect of total trade, the United Kingdom has therefore made the greatest progress in the year 1913, but in percentage proportion, German foreign trade has grown more last year than has British trade. The increase in the turnover with foreign countries of the United States in 1913 was very much less than that of Germany and Britain, smaller even than that of France. It is not surprising that the imports of the United States should have fallen off after the exceptionally large increase in this department in the year 1912 (as a result of the impending changes in the Tariff), rather is the fact worthy of notice that the diminution has not been greater, because experience shows that the decline of a trade-boom in that country is usually accompanied by a pronounced restriction of imports. The circumstance that in Germany, too, the imports have shown scarcely any increase in the year 1913 is probably chiefly attributable to the good harvest, but also of course to the restriction in the purchases of raw material which was the concomitant of the decline from boom conditions. The state of affairs has been similar, although it has not been so unfavourable, as in the year 1908 and 1901, two years of economic crisis, in which a decrease of imports was recorded in Germany.

It is interesting to notice that, immediately following the four leading commercial powers, the Netherlands take the fifth place in respect of foreign trade. Calculated per head of the population, this small country, partly as a result of its busy transit-trade, holds by far the greatest foreign traffic, nearly three times as much as Britain and five times as much as Germany. Next in order, so far as figures are at present available, come Belgium, India, Austria-Hungary, Russia, Italy, Argentina and Canada.

The harvest of 1913 was good in almost all countries. For example, the world's wheat crop reached 108 million tons, as compared with 102 million tons in 1912 and 95 million tons in 1911. The world's output of oats was 70 million tons, compared with 68 million tons in 1912 and 75 million tons in 1911. That of barley was 35 million tons, compared with 33 and 31 million tons. In rye alone the world's crop was a little less than in 1912 (49 against 50 million tons), but even this is to be regarded as exceedingly good, seeing that the previous year's crop was admittedly a brilliant record. The maize-crop showed a falling off as compared with 1912, because of a great shortage in the United States.

Now the fact of very good crops having followed upon equally good ones in the preceding year, has tended to restrict the total commerce of the world, because the necessity for importing cereals (always a large item in the statistics) was smaller in the consuming industrial countries in proportion as their own output of cereals was increased.

According to the report of the Berlin Chamber of Commerce[1]) the figures relating to the foreign trade of the German chemical industry showed considerable increases last year. The exports of chemical and pharmaceutical products, dyes and dye-stuffs rose from 41,7 million double cwts. in the year 1912 to 49 million double cwts. The fear which was felt at the beginning of the Balkan war that the chemical industry especially would have to look for a decline in business, because it is so largely interested in the export trade to the Balkan countries, and, most of all, to Austria-Hungary, has only been partly confirmed. The falling-off due to the paralysis of industry in the countries named was counterbalanced by an increase in the shipments to other parts. The exports of aniline dyes to China and British-India showed a particularly noticeable advance. The imports of chemicals of all kinds, however, have not kept pace with this increased activity in exports. They only amounted to 20,6, as compared with 19,3 double cwts. in the previous year.

Dyes and dye-stuffs especially showed a decline.

With regard to essential oils the figures are as follows[2]): —

Imports in the year	1913	1 566 000	kilos, value	ℳ	24 603 000.—,
„ „ „ „	1912	1 578 400	„	„	„	24 818 000.—,
Exports „ „ „	1913	1 073 900	„	„	„	15 661 000.—,
„ „ „ „	1912	725 500	„	„	„	9 650 000.—.

These figures clearly show the marked increase in exports.

With regard to imports, the quantities were as follows: —

	1913	1912
Lemon-, orange-, bergamot- and other *Citrus* oils from Italy	179 100 kilos	200 500 kilos
Camphor oil, menthol and peppermint oil from Japan . .	503 700 „	690 600 „
Cassia- and star anise oils from China	184 000 „	145 400 „
Peppermint oil and other oils from U. S. A.	137 400 „	190 200 „ .

[1]) *Berliner Jahrbuch für Handel u. Industrie* **1913**, I, 57. — [2]) *Statistisches Warenverzeichnis*, No. 353 b/c.

The quantities of essential oils exported from Germany, by countries of destination, in the last three years have been as follows: —

	1913	1912	1911
France	102 100 kilos	77 600 kilos	52 500 kilos
U. Kingdom	114 700 „	68 200 „	72 500 „
Italy	28 000 „	31 600 „	26 000 „
Austria-Hungary	90 200 „	70 000 „	62 300 „
Russia	99 600 „	74 500 „	77 400 „
Spain	46 900 „	35 400 „	15 800 „
Japan	41 100 „	36 000 „	32 900 „
U. S. of America	271 100 „	129 300 „	95 400 „ .

The statistics of the quantity and value of the imports into and exports from Germany of essential oils in the last seven years are set forth below: —

IMPORTS.

	1913	1912	1911	1910	1909	1908	1907
Kilos	1 566 000	1 578 400	1 251 500	1 524 300	757 800	911 300	1 498 600
Value ℳ	24 603 000	24 818 000	17 808 000	15 068 000	11 528 000	9 590 000	10 238 000

EXPORTS.

Kilos	1 073 900	725 500	595 800	547 600	512 600	390 800	491 700
Value ℳ	15 661 000	9 650 000	8 087 000	6 298 000	5 184 000	5 287 000	6 883 000

The foreign trade in artificial odoriferous substances[1]) was as follows: —

IMPORTS.

	1913	1912	1911	1910	1909	1908	1907
Kilos	22 500	18 400	17 300	17 900	16 100	11 300	11 300
Value ℳ	439 000	359 000	338 000	348 000	316 000	259 000	236 000

EXPORTS.

Kilos	673 000	578 800	493 100	427 000	417 100	280 000	279 400
Value ℳ	6 289 000	5 122 000	4 905 000	512 800	4 158 000	3 161 000	2 822 000

The exports of artificial odoriferous substances to the three principal foreign markets in the last three years were as follows: —

	1913	1912	1911
France	78 500 kilos	61 100 kilos	45 600 kilos
U. Kingdom	102 700 „	95 900 „	81 800 „
U. States	184 200 „	165 600 „	132 800 „ .

These figures explain themselves. They afford a clear review of the splendid development of our industry during the period referred to, and of its increasing importance as a factor in the world's trade.

Notwithstanding the serious contraction in output suffered by the chemical industry of Austria-Hungary last year, the prime cause of which, no doubt, was to be sought in the strained relations with Russia, our Bodenbach branch firm was very well occupied. The orders received there were so many that there was little to be perceived of any economic crisis, and the deficiency caused by the almost complete cessation

[1]) *Statistisches Warenverzeichnis*, No. 354.

of activity in the soap-industry was compensated by increased demand in other departments. The law regulating the Excise Duty on Alcohol which had so long been expected, was enacted on 23rd January 1914, and came into force on February 1st. Under its provisions the excise duty on alcohol established by the law of 8th July 1901 has been increased, the manufacturing-duty and the duty payable on sale for consumption (lower scale) being raised to 1.40 Kronen per liter alcohol and the duty on sale for consumption (higher scale) to 1.60 Kronen per liter alcohol. Although this new tax constitutes an unpleasant burden for the liqueur-industry, which is not very prosperous in any case, yet it cannot be said that the increased tax oppresses this branch to such an extent as was often stated to be the case in the press before the tax was enacted. Moreover, concurrently with the increase in the excise the Austrian spirit-trust reduced its selling prices, so that the price-raising effect of the law was largely counteracted. To give an example, we have found it possible to leave the prices of by far the greater part of our alcoholic essences unchanged.

The import- and export-movement of essential oils in the Austro-Hungarian Monarchy during the last two years has been as follows: —

IMPORTS.	1913	1912
Laurel-, rosemary-, juniper- and light camphor oil . .	20 200 kilos	15 900 kilos
Essential oils not especially enumerated	109 900 „	95 800 „
Essential oils and fruits of the *Citrus*-family	19 500 „	23 300 „
Bitter almond oil, cajuput oil, melissa oil, peppermint oil, sandalwood oil, sassafras oil, mustard oil and cedar wood oil	40 700 „	36 900 „
	190 300 kilos	171 900 kilos

EXPORTS.	1913	1912
Laurel-, rosemary-, juniper- and light camphor oil . .	32 600 kilos	22 400 kilos
Other essential oils	51 800 „	44 700 „
	84 400 kilos	67 100 kilos

According to the December-issue of the Statistical Returns relating to the foreign trade of the Austro-Hungarian Monarchy[1]), the commercial balance of the year 1913 closes with an excess of imports over exports of 516,5 million Kronen, showing an improvement of 226,5 millions compared with the previous year, when the balance on the same side was 743 millions.

The increase of our trade with France last year was so great as to constitute a record, and we mention this fact with the greater pleasure because competition is exceptionally keen in this very receptive market. We see in it fresh proof that the French perfumery industry, which means the industry of the connoisseurs in our branch of trade, fully appreciates our efforts to supply only the best of the best. We shall know to honour the confidence of these customers in the future as we have done in the past.

We are informed by the Central Bureau for the preparation of Commercial Treaties that according to the returns for 1913 supplied by the General Direction of the French Customs, the imports into France from Germany in that year reached a value of 1074 million francs, and French exports to Germany a value of 869 million francs. As compared with the preceding year, therefore, the imports from Germany have risen

[1]) *Nachr. f. Handel, Ind. u. Landw.* **1914**, No. 19

by 75 and the exports to Germany by 47 millions. These figures as here presented give the impression that the development has been exceedingly favourable for Germany, but when we look into details, and especially when we examine in what directions the French trade of Germany has grown, the picture changes. The excess of imports from Germany as compared with the previous year consists principally of agricultural produce. French imports of cereals from Germany amounted to 94,3 millions, as compared with only 25,7 millions in the previous year. This item alone shows a gain which almost equals that of the total increase of imports. On the other hand, manufactured articles show a long list of decreases. French imports from Germany fell in ceramic products from 44 to 37 millions, in cotton tissues from 28 to 25, in linen underwear and other articles of clothing from 5 to 3, in manufactured furs from 46 to 38, in genuine jewelry from 9 to 6, in sham-jewelry from 39 to 36 million francs. The imports from Germany have also decreased in the following departments: iron and steel, yarn, tissues of silk and wool, leather, watches, furniture, prepared colours, rubber goods, meerschaum goods and beer.

In the case of most of the articles enumerated above there has never previously been any sign of diminished imports from Germany; it follows therefore that the measures which have lately been applied by the French Customs Department have not failed to be effective, and have seriously injured German export industry.

The imports into and exports from France of essential oils and synthetic perfumes during the last three years have been as follows: —

ESSENTIAL OILS:

Imports	1913	844 500	kilos	value	Fr.	2 827 100.—,
„	1912	959 500	„	„	„	2 880 500.—,
„	1911	938 900	„	„	„	2 687 600.—.
Exports	1913	1 426 600	„	„	„	33 812 600.—,
„	1912	1 688 400	„	„	„	38 740 000.—,
„	1911	1 655 300	„	„	„	32 802 000.—.

SYNTHETIC PERFUMES:

Imports	1913	113 300	kilos	value	Fr.	1 378 000.—,
„	1912	99 000	„	„	„	1 424 000.—,
„	1911	103 500	„	„	„	1 372 000.—.
Exports	1913	14 800	„	„	„	164 000.—,
„	1912	51 900	„	„	„	192 000.—,
„	1911	22 300	„	„	„	168 000.—.

A comparison of these figures with those relating to quantities and values for Germany (p. 9) offers many points of interest.

Mention also deserves to be made of the fact that the vexatious practices of the French Customs officials, to which we have repeatedly referred in the past, have fortunately been abated to some extent lately, although occasionally unfounded objections and, as a result thereof, disagreeable delays in the dispatch of goods, still occur. It is to be hoped that a knowledge will soon spread in French commercial circles of the fact to which the present French Under-Secretary of the Mercantile Marine, M. Maurice Ajam, calls attention in his excellent book *"Le Problème économique franco-allemand"*. M. Ajam points out that in spite of the stirring-up of the chauvinist press, German imports of French merchandise have risen from 860 millions in 1910 to

981 millions in 1912, and that "unfriendly" Germany has now reached a point when it buys exactly ten times as much from France as does friendly and allied Russia[1]).

As will be seen from the statistics published on p. 9, the German exports of essential oils and synthetic perfumes to England have also shown a considerable increase in the course of last year, and of this our London branch house may claim an important share. Notwithstanding the persistence of many obstacles connected with home-politics, the conditions of sale in almost all branches of industry have been extremely favourable. Owing to the opportunities of expansion which are open to it in the Colonies, the economic life of England is so healthy and so strong that very different causes than those described above would be needed to obstruct the onward course of the industry and commerce of this country. The apparent necessity in which certain German firms found themselves during the opening months of the new year of improving their embarrassed financial position by the sale of large parcels of commodities, has again shown up in its true colours the price-cutting which is rife in our industry. England is a favourite ground for such "transactions of necessity" because the conditions of payment obtained in the country make it possible to turn merchandise into cash there more quickly than anywhere else. Several transactions of this kind have come to our knowledge in which the buyers concerned suffered disappointment in the end, because the question of quality gave rise to discussions which will probably result in the sellers selecting a fresh field for their financial operations in the future.

The annual report for 1913 of the Liverpool firm of Bigland, Sons and Jeffreys[2]), dealing with several staple articles of commerce, has the following reference to the British soap trade, and to certain subjects related thereto: —

"British exports of soap further advanced in the year 1913 as compared with the year 1912, as they had done in the year 1912 compared with 1911. But the increase from 1911 to 1912 (from 82443 tons to 87602 tons), was larger than that from 1912 to 1913 (87602 tons to 89334 tons). This is due to the conditions of the year 1913 (Balkan war, fears of a great European war, high rate of interest, restriction of enterprise), which unfavourably affected even Great Britain. In sympathy therewith, too, the imports of soap, which had risen in 1910 to 1911 from 17017 tons to 19127 tons, and in 1911 to 1912 from 19127 tons to 24338 tons, fell in the year 1913 to 22144 tons. This decrease chiefly affects soap stock, of which the imports showed a decline of from 4282 tons to 2450 tons, whereas the imports of soap powder, washing soap and toilet soap actually showed increases. In the export department, the figures for soap powder fell from 1524 tons in the year 1912 to 1245 tons in the year 1913, while at the same time the exports of washing soap rose from 79259 tons to 81251 tons and those of toilet soap from 4120 tons to 4260 tons.

In the year 1913 the imports of the hitherto customary raw materials for soap-making, such as tallow, palm oil and cocoa-nut oil showed a drop of more than 6000 tons. But it must not be concluded from this that the production of British soaps decreased in that year, because the new hardening process has also given to certain other fatty substances, such as whale oil and linseed, which formerly were scarcely of any account, a great importance for the soap industry. This process is all the more important for the British soap industry because through the establishment of numerous soap factories in countries which formerly supplied basic materials (South Africa, Australia, Argentina, Japan, &c.), these materials are now employed locally

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[1]) *Deutsche Export-Revue* **1914**, No. 12. — [2]) *Handelsmuseum* **29**, No. 12.

instead of being sent to Great Britain. Thus the hardening process has prevented an enhancement of the prices of the basic materials, and of the soap itself, which would have considerably restricted both the consumption and the production.

The extent to which the use of soap is increasing in all civilized countries may be judged from the example of the United States. The Census of Production in that country for 1904, published in 1905, showed a production of 605000 tons, while the Census for 1909, published in 1910, gave as much as 775000 tons, that is to say an increase by weight of 27,4 p.c. corresponding to an increase in value of as much as 54,8 p.c. Without the additional sources for the supply of basic materials which have been newly disclosed by the progress of chemical technology the production would have been unable to keep pace with the requirements of the consumption. According to the results of the two North American census years which have been quoted, the consumption of tallow in that country decreased between 1904 and 1909 by 27679 tons, and that of caustic soda by 19000 tons, while in the same period the consumption of cocoa-nut and palm-oil increased by 20000 tons, of cotton seed oil by 44000 tons, of rosin by 17857 tons, and so on. The utilization of linseed oil has become of increasing importance for the soap industry of the United States, as for that of all other countries."

We reproduce this article in full, because it will no doubt greatly interest our readers among the soap manufacturers.

The conditions governing the sale of our manufactures in Australia have been normal. In view of the fact that the climatic conditions have everywhere been favourable, and especially because rains have not been wanting, an abundant wheat crop is expected, and sheep-farming also has progressed favourably. It may therefore be taken for granted that these factors will have the effect of increasing the purchasing power of the people.

In British India, however, a different state of affairs prevails. Business, which has been brisk, is now growing somewhat duller, mainly owing to the failure of the so-called winter rains, which usually set in in India towards the end of December, but which this season have either been wanting, or have been insufficient, over almost the whole of the country. In many districts the crop has been a complete failure. This applies especially to the United Provinces of Agra and Oudh, and to certain districts in the Presidency of Bombay[1]) where it is said that in some parts the condition of things is very bad indeed. Throughout an area in the United Provinces covering 17000 sq. miles, with a population of over five millions (equal to the population of Australia), there is said to be great distress, while over a further area of 30000 sq. miles, with a population of 14 millions, the prospects are described as being but little better. In many districts the peasants are said to be selling their cattle cheaply, while in other parts, for want of fodder, comparatively large numbers of cattle are reported to be dying of hunger. The Government has already ordered the carrying out of relief-works, such as the making of canals and roads, in order to provide work and sustenance for the population. This is always done in similar cases in order that the people may have a chance of providing a livelihood, at any rate to some extent, for their families. Of course the districts which have been afflicted by distress up to the present constitute only a small proportion of the country, both in respect of area and of population, and although the local significance of the famine is very serious, the further course of events must be awaited before general conclusions can be drawn. It is yet too early to express an opinion whether the distress will

[1]) *Nachr. f. Hand., Ind. u. Landw.* **1914**, No. 24.

assume wider dimensions and will extend to other districts, or what effect it will have upon the neighbouring provinces.

The financial crisis at the close of 1913, too, has not yet been overcome. A few well-known but badly-established and in part adventurously-conducted native banks in Bombay failed, causing widespread injury and severely shaking commercial confidence.

The expectations of a favourable development of business in Spain, to which we gave expression in our last *Report,* appear to be in course of fulfilment, at any rate so far as the branches are concerned in which we are interested. It is true that many general complaints are still heard to the effect that trade continues to drag owing to the pressure of insecure political conditions and the still unsettled Morocco-affair, but so far as our experience goes we can only say that our turnover during the winter months of 1913 and the first months of the present year show a steadily increasing tendency. The olive crop of last winter has been good, and in part even excellent, a fact which is of the greatest possible importance for the course of business in all branches, especially in the Southern Provinces. A further favourable development of trade and industry is therefore probable.

As we have already prophesied, the negotiations between the French and Spanish Governments have been limited to the drawing up of a joint plan of action in Moroccan politics; no alliance, such as was much talked of in the daily press at the time, has been concluded, and international commercial relations with Spain have therefore undergone no change.

Soon after the publication of our last *Report* the Liberal Ministry fell, and was compelled to make room for a Conservative Government. But in the meantime the Conservative party has also been split up into two sections, at the head of one of which is the old Conservative leader Sr. Maura, while the control of the other is in the hands of the Prime Minister, Sr. Dato. Internal disunion, which at the time brought about the overthrow of the Liberal party, therefore now reigns also in the Conservative camp, and naturally the country suffers from the consequences of these aimless, selfish party quarrels.

There has scarcely been any alteration in the condition of business in Italy, but it cannot be denied that there is perceptible in this market a brighter feeling, which dates from the close of the war. It is true that the export of essential oils from Germany to Italy has declined somewhat (see the table on p. 9), but it would not be fair to conclude therefrom that there has been a falling-off in the demand. Our own shipments to Italy at any rate, have increased both in respect of value and of quantity.

So far as statistics are available at present, the total imports from Germany into Italy, as compared with the figures for 1912, show an increase of 13,8 million Lire, and the exports from Italy to Germany an increase of about 8,4 million Lire.

The value was as follows: —

	Imported from		Exported to	
Germany	612,5	Million Lire	336,7	Million Lire
United Kingdom . . .	601,1	„ „	261,1	„ „
United States	505,6	„ „	257,7	„ „
France	280,9	„ „	230,9	„ „
Austria-Hungary . . .	264,1	„ „	218,8	„ „
Argentina	173,9	„ „	190,3	„ „
Switzerland	38,5	„ „	248,6	„ „

Germany, therefore, maintains indisputably the first place in the total foreign trade of Italy.

Business in Russia was more than ever affected last year by embittered competition among the German firms in our branch of trade, whereby satisfaction with the increased turnover which was effected was seriously curtailed. It is especially to be regretted that many Russian customers, in their anxiety to buy cheaply, attach altogether subsidiary importance to the question of quality. The nefarious consequences of these tactics are bound to make themselves felt sooner or later. According to communications from the Commercial Treaties Union[1]), the extraordinarily thorough preliminary work in connection with the coming commercial treaties which is being carried out by the various Ministries and other authorities, is by no means approved in interested circles in Russia. Between the different administrative departments there are standing jealousies at work, rendering profitable co-operation impossible and, in fact, making it questionable whether a proper preliminary drafting of the Commercial Treaties will be practicable at all. There is, in particular, acute antagonism between the Ministries of Commerce and of Agriculture. One of these departments has recently prepared a secret memorandum in which it accuses the other of having turned the preparations for the treaty into a wrong channel, and of representing industrial interests in an entirely one-sided manner. Further, the secrecy of the politico-commercial intentions of the Russian Government, which it was desirable to preserve, had been jeopardized by admitting private organizations to official conferences. It is suggested that a special, purely national authority shall be created which shall not be subject to any Ministry.

From the German side the taking of expert-evidence on the part of several organizations of which the members are interested in trade with Russia, has already begun. As the desires of the German essential oil and perfumery industry are in general agreement with those of the Russian firms which use our manufactures, it is probable that the result of the revision of the Russian Tariff, so far as these industries are concerned, will be satisfactory.

Now that peace has been re-established in the Balkans, the business life of Roumania, which had naturally suffered from the effects of the war, again moves within ordered lines. The financial situation of the country is thoroughly satisfactory and the economic condition of the people inspires every confidence, the harvest having been extremely good. The purchasing power of the agricultural classes, who were the first to profit by the bountiful crops, has rarely been so great, and the natural result is that commerce and industry are enjoying an increased turnover. With the object of opening-up the newly-acquired territories, road-making has been taken in hand as the first task, and the carrying-out of the programme of improved communications will afford wide opportunities for labour and for the earning of wages in the future. The good impression which has been created abroad by the attitude of the Roumanian Government during the Balkan war has increased the self-confidence of the people, and has spurred it on to deepen this impression still more. Mistakes may, of course, be made in these efforts from time to time, as witness an order promulgated by the General Commission of Customs last December, by which agents and commission-houses are forbidden to import and to deal in essential oils and colours used as condiments and as dyes for comestibles and beverages, and wherein the right to carry on this trade is restricted to a few factories which are mentioned by name, and to the druggists of the country. This order is all the more surprising because it has been the earnest endeavour of the Roumanian Government during the last few years to do everything in its power to foster native commerce and industry.

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[1]) *Deutscher Aussenhandel* **14**, No. 5.

The decisions of the Board of Hygiene, to which samples from every consignment of the articles in question must be submitted by the Customs, even when the goods are addressed to firms which are entitled to import them, also give rise to frequent complaints. The fact that goods are sometimes unjustly condemned is not exactly calculated to show the technical knowledge of the chemists responsible for their rejection in the best light.

From Bulgaria also, a vigorous improvement in business and an increased demand for our manufactures can be reported since the conclusion of peace. The *Levante Zeitung* of January 1st reports as follows on the state of trade at the close of the year:

"Now that three months have passed since the termination of the Moratorium, it may be stated that in regard to solvency Bulgaria has shown itself in every respect worthy of its good reputation. Notwithstanding the difficult situation created by the long duration of the state of war, and the unfavourable outcome of the campaign against Servia, Greece and Montenegro, current liabilities are on the whole being discharged punctually, even when it is admitted that foreign creditors, acting in conjunction with the local banks, and taking into account the exceptional conditions, have shown themselves accommodating in the highest degree. The increase in the agio rate to 14 p. c. is a great calamity, because it causes the merchants great losses, especially for liabilities of old standing, and they are unable to recoup this loss. For this reason business is still generally at a standstill, particularly so because it is impossible to foresee clearly, even for the immediate future, what will be the results of the new election for the Sobranye upon the economic position of Bulgaria. In the meantime the exportation of corn has begun, although for the present it is on a small scale, but no complete relief can be expected for the local money-market until a large loan has been concluded. Hence the attention of the whole commercial world of the country is now concentrated upon the steps which are being taken by the Government in this direction, and in the interest of a rapid and healthy improvement in the commercial relations with Bulgaria it is to be hoped that these efforts will soon lead to a satisfactory result. The delay in the handling of imported goods by the Customs- and Railway-Authorities, due to the war, is slowly undergoing improvement. The healthy foundation upon which the economic conditions of Bulgaria are reared, and especially the thrifty and sober character of the Bulgarian farmers, warrant the hope that the country will overcome the injurious effects of the war more rapidly than any other Balkan state.

The difficulties in transportation continue to be a heavy burden on trade. The railways suffer from a chronic shortage of rolling stock, and this will need to be removed before communications with foreign countries can be put on the footing which is desirable in the interests of a regular exchange of commodities. So far the crop-prospects are quite favourable, and the agricultural section of the population should therefore rapidly recover from the effects of the war."

The fact that the revival of the exchange of merchandise with Servia is making slow progress must also be ascribed to the interruption in communications. When the railways had finished their work in connection with the demobilization of the Army, they were faced by the task of conveying the masses of merchandise that were waiting to be passed through the Customs at the frontier stations, and this task was soon found to be impossible of accomplishment owing to lack of rolling stock. As late as the middle of February 1400 wagons loaded with all kinds of imported merchandise were standing in the goods' yards at Belgrade, this accumulation being caused through the want of a sufficient customs- and railway-staff. It is due to the energetic

action of the Minister of Finance that the parcel post communication with foreign countries at any rate is conducted with some approach to punctuality, and until order has been restored in railway traffic the international exchange of goods will remain dependent upon this insufficient branch of the transport-service. It is to be hoped that the prevailing chaos will soon be removed, for until this is done there is no possibility of any profitable development of trade with Servia.

In connection with the rumours of the projected new political Balkan alliance, reports are constantly cropping up again of a Customs-Union of the Balkan States[1]). So long ago as the year 1907 such a Union had been projected between Servia and Bulgaria, but it has never been realized. Similarly, all more ambitious schemes have so far proved abortive, and it is hardly likely that there will be any chance of their realization so far as can be foreseen. The only arrangement which may perhaps be carried out in the near future is a customs- and railway tariff convention between Servia and Greece. It is said, in fact, that a customs-convention is already being drafted. There is also a project of creating a bonded-zone for Servian goods at the port of Salonica, within which Servian commerce will enjoy far-reaching privileges. The Greek Government is also credited with wishing to conclude treaties with Roumania and Austria-Hungary. Negotiations for a treaty between Bulgaria and Turkey have already been pending for a long time.

Turkey, after her defeat in the war, is gradually beginning to recover from its misfortunes, and the prospects for the sale of our goods have improved again during the last few months, since the conclusion of peace with Greece has at length restored quietness in the political situation of the Ottoman Empire after a disturbance lasting over two years. The chief task now before Turkey is to succeed in also restoring healthier conditions within the country itself, for it is evident that the present unrest must seriously damage credit. Since her heavy losses of European territory to the victors, the centre of gravity of Turkish interests has shifted to Asia Minor, which country may in future acquire a similar importance for the peace of Europe as the Balkan Peninsula has possessed in the past, seeing that all the Great Powers have interests there.

According to the "*Aussenhandel*"[2]) the territory which has been lost to Turkey by the conclusion of peace is divided among the several victorious States in the following proportions: —

	1000 Sq. Kilometres.		Millions of inhabitants.	
	before the war	now	before the war	now
Bulgaria	96	120	4,3	5
Greece	63	108	2,6	4,2
Roumania	131	139	7,25	7,50
Servia	48	90	3	4,1
Montenegro	9	16	0,25	0,50
Albania	—	32	—	0,85

Egypt has also suffered indirectly through the Balkan war, which followed close upon the unrest caused to it by the war in Tripoli. The calling-up of Greek merchants to the colours, monetary sacrifices in favour of Turkey, suspension of trade with Syria, diminution in the number of visitors from abroad, all these factors have impeded the development of trade last year.

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[1]) *Deutscher Aussenhandel*, **14**, No. 5. — [2]) XIV. No. 2.

In 1913 the Egyptian imports reached a value of 27865195 £E. compared with 259075759 £E. in 1912. On the other hand the exports amounted to only 31662065 £E. compared with 35474321 £E. in 1912. The cigarette-industry figures in these returns with a reduction of 30000 £E. In the imports, England of course takes the lead, with 8496483 £E. Germany has receded from the fifth to the sixth place, although its total turnover was larger than in the previous year: 1608881 £E. against 1421180 £E. in 1912. The British Colonies have taken the fifth place. The reason of this is in the first place the steady growth of the exportation of food-stuffs and pulse from India to Egypt and the Soudan, and also the continued advance in the imports of Indian manufactured goods. A reduction of imports has taken place in skins, leather and leather goods, colonial produce, stoneware, glass, china and crystal, dye-stuffs, chemical products and medicines. There were increase in the imports of grain and vegetables, flour, spirituous preparations, beverages and oils, paper and books, coal, timber, textiles and metal goods. In the export department there have been reductions in cotton, rubber, sugar, fruits and vegetables.

The somewhat unfavourable state of business was naturally attended by occasional suspensions of payment, but since the disturbing elements have been removed by the conclusion of peace, there is no longer any ground for anxiety as to the future of trade with Egypt.

According to statements by "Bradstreet's" the value of the total exports of the United States of America, as well as the total value of foreign trade of the country, surpassed all figures of previous years, while the active side of the commercial balance shows an equally striking growth. On the other hand, the value of the imports of merchandise remained below that of the preceding years, notwithstanding that the new customs tariff, with its numerous reductions in duties, was already in force during the concluding quarter of the calendar year, and the importations of food-stuffs, principally meat and maize, from abroad reached a volume never known before. Although the falling-off in the imports caused surprise in many quarters, the increase in exports was not unexpected. The value of the total exports reached 2484 million $, and exceeded that of the previous year, which constituted a record, by 3,5 p.c. The imports only reached a value of 1792 million $, or 1,8 p.c. less than those of 1912, the leading import-year on record. The value of exports and imports together was 4276 million $, or 1,4 p.c. greater than the total for 1912; the excess of the value of exports over imports was 692 million $, which was greater by 56 millions than the result of 1907/08, the previously most favourable commercial year.

The figures relating to the foreign trade of the United States during the last 10 calendar years are as follows: —

Year	Imports	Exports	Total foreign trade	Excess of exports
	Value in Millions of Dollars			
1913 . . .	1792	2484	4276	692
1912 . . .	1818	2399	4217	581
1911 . . .	1532	2092	3624	560
1910 . . .	1563	1866	3429	303
1909 . . .	1475	1728	3203	253
1908 . . .	1116	1753	2869	637
1907 . . .	1423	1923	3346	500
1906 . . .	1320	1798	3118	478
1905 . . .	1179	1626	2805	447
1904 . . .	1036	1451	2487	415

Our New York branch house sends us the following report of business in its own branch of commerce during the year 1913: —

"We remarked in our report of October 1913, that the last few months of the period under review showed a somewhat forced business on account of the impending tariff revision, a condition which remained also *after* the enactment of the new tariff, for the simple reason that all business houses continued to provide their regular trade with duty-free goods as long as their stocks lasted, and since the stocks were, as a rule, rather ample, we may say that the entire last half of the past year has stood under the influence of the new tariff.

The extraordinarily large business which marks the year 1913 has, therefore, at least partly to be attributed to the above outlined singular conditions and it had further to be expected that a certain retrogression in business would naturally take place during the first months of the new year. That this recession has been only slight in our particular case is again a sign of the perfectly healthy condition of our business, and, besides, the natural consequence of the strict tendency on our side not to encourage speculative utilization of the apparent advantages brought about by the new tariff regulations, which, in this way, could easily become a pitfall for the speculator.

Speaking about the influence the new tariff has had on the various industries in which we are specially interested, we may repeat from our report of April 1913 that we expected "American trading and manufacturing circles, which had solved harder problems in the past, would find ways and means to overcome the impending difficulties and to adjust themselves to the given conditions". And so it has come.

Judging from our intimate relations with the three main groups of trade on which our business depends, the Manufacturing Perfumery, Soap and Flavouring Extract industries, we may safely state that the greater burdens which the new tariff has imposed upon them are not showing any detrimental influence, — business has simply adjusted itself to the changed conditions.

A spontaneous and very material help in this connection must be ascribed to the fact that the price formation of many of the most important staple commodities has been such during this period, that the increase in price, caused by the newly imposed duty, was entirely counterbalanced by their retrogressive price development. So Oils, like cassia, lemon and orange, have sold after the enactment of the new tariff at actually lower prices than at the time before the enactment, under a duty-free entry into the United States.

The price formation during the current year has, as above indicated, so far been generally in favor of the buyer. Some commodities have taken actual slumps in prices, as, for instance, the Messina Essences: lemon and orange. Also the different grades of geranium oil and most of the specifically American oils have shown a downward tendency in price. This condition has, to a certain extent, influenced the contract business in the beginning of the year, which, with an upward tendency of the market, would naturally have shown a more lively character. In this connection we may also state that we have made it our steadfast policy, in the interest of our patrons, not to encourage contracting, when the tendency of the market would point to lower prices later on in the season. The aggregate of the contract business has, however, been perfectly normal, though same has been drawn out over a longer period than usual. It is true that the last year has set a very conspicuous pace of progress in business, but we nevertheless expect to keep up with the further development at an equal rate of expansion. This expectation is based upon the presumption

that general business conditions, which have shown a certain abatement on account of a rather reserved attitude during the last few months, will again assume a normal and prosperous aspect, as soon as the benefits of the installation of a central banking system after the pattern of the Bank of England or the *Deutsche Reichsbank* will be fully understood. The only possible danger which may befall American business, we see in the Mexican tangle, from which further serious complications may arise at any minute.

A recent action of the new Secretary of Agriculture, Houston, seems to be destined to make quite some change in the administration of the Pure Food Law. The Secretary ordered the dissolution of the so-called Board of Food and Drug Inspection which was originally created by the former Secretary Wilson for the purpose of curtailing the administrative power of the Chief Chemist, which position was in the hands of Dr. Harvey Wiley at that time.

This three-cornered administrative body has been, during its entire life, an impediment to quick and effective working methods of the Bureau of Chemistry, and its removal will therefore be welcomed by all those interested in the efficiency of this Department. It is quite correct that this action entrusts the present Chief, Dr. Alsberg, with an almost unrestricted power in reference to pure food matters, but since this official has so far shown wise judgment in the application of the law in all his actions, trade circles expect that this change will work to their best interest.

As had to be expected, the regulations of the new Tariff Act give rise to numerous controversies between the official circles and the importers in regard to their proper application. So particularly paragraph 49 of Schedule A, which provides a 20 % *ad val.* duty on several enumerated articles, continuing: "and all natural or synthetic odoriferous or aromatic substances, preparations, and mixtures used in the manufacture of, but not marketable as, perfumes or cosmetics", has proved to be a veritable source of greatly diverging opinions as to the underlying intention of the framer of the law in regard to the articles falling under its scope. The customs officials claimed that any article, no matter what its general nature or characteristics might be, would be properly covered by this paragraph, if it could be directly or indirectly used as a basic material for the production of an accessory in the manufacture of perfumes or cosmetics. In accordance with this official conception, articles like sandalwood in logs, orris root, lavender flowers, etc., have been assessed by the appraisers of merchandise at 20 % *ad val.* duty, while the same articles have so far always been classified as vegetable drugs, enjoying either duty-free entry or a duty of only 10 per cent *ad val.* if in a condition of advanced value.

A vigorous protest against the above mentioned classification has been entered by the affected trade circles and a recent Treasury Decision issued to the Collector of Customs of the Port of New York reverses the official conception and upholds the dissenting opinion of the importers.

Our Canadian business has not fully kept up with the remarkable development of last year's progress in the United States. This may be attributed to two main reasons. First, there has not been the stimulating influence in Canada which the new Customs Tariff exerted on the United States business, and, secondly, it seems that the last year has brought a certain standstill in business in the Dominion, after the extraordinary activity during the last few years, which has not been devoid of an overspeculative tendency that was fraught with all the elements of a timely reaction. This seems, however, to have been more especially confined to the real estate market, and has not seriously affected general trade conditions. We are, therefore, justified

Value of imports and exports of Essential Oils from and into the United States, in the second half of the years 1913 and 1912 respectively.

	Imports			Exports	
	1913	1912		1913	1912
July	duty-free $ 455 612	$ 104 415	July	Peppermint Oil $ 16 284	$ 28 793
	dutiable „ 62 927	„ 49 926		Other indigenous Oils „ 19 428	„ 24 282
				Foreign Oils, duty-free „ 4 363	„ 6 115
				„ „ dutiable „ 8 484	„ 1 567
August	duty-free „ 297 631	„ 292 200	August	Peppermint Oil „ 12 994	„ 12 605
	dutiable „ 82 916	„ 92 802		Other indigenous Oils „ 19 392	„ 26 587
				Foreign Oils, duty-free „ 2 712	„ 3 179
				„ „ dutiable „ 6 259	„ 3 222
September	duty-free „ 354 710	„ 281 895	September	Peppermint Oil „ 49 849	„ 27 271
	dutiable „ 115 150	„ 84 595		Other indigenous Oils „ 15898	„ 18 355
				Foreign Oils, duty-free „ 8 212	„ 1 739
				„ „ dutiable „ 2 330	„ 6 055
October	duty-free „ 4 443	„ 357 216	October	Peppermint Oil „ 107 078	„ 92 449
	dutiable „ 130 047	„ 81 331		Other indigenous Oils „ 28 783	„ 45 873
				Foreign Oils, duty-free „ 5 938	„ 2 824
				„ „ dutiable „ 6 450	„ 7 520
November	duty-free „ 2 018	„ 150 497	November	Peppermint Oil „ 45 043	„ 69 760
	dutiable „ 128 462	„ 106 356		Other indigenous Oils „ 16 940	„ 51 944
				Foreign Oils, duty-free „ 2 837	„ 1 352
				„ „ dutiable „ 4 792	„ 3 020
December	duty-free „ 3,273	„ 262 914	December	Peppermint Oil „ 17 812	„ 46 710
	dutiable „ 209 061	„ 101 667		Other indigenous Oils „ 14 858	„ 19 239
				Foreign Oils, duty-free „ 2 477	„ 3 937
				„ „ dutiable „ 2 877	„ 4 878

Total value of imports for the 2nd half-year	1913	$ 1 846 250
„ „ „ „ „ „ 2nd „ „	1912	„ 1 965 814
„ „ „ „ „ „ whole year	1913	„ 5 619 921
„ „ „ „ „ „ „ „	1912	„ 4 116 641
Total value of exports for the 2nd half-year	1913	$ 422 090
„ „ „ „ „ „ 2nd „ „	1912	„ 509 276
„ „ „ „ „ „ whole year	1913	„ 748 105
„ „ „ „ „ „ „ „	1912	„ 850 923

in expecting a further steady development of our Canadian business connections during the current year."

Thus far the report of our New York friends. In perusing the table dealing with the imports and exports of essential oils into and from the United States, it must be remembered that the new Customs Tariff Law came into force on October 4, and that consequently from that date the relation between the essential oils imported duty-free and those which are dutiable assumed altogether different proportions in respect of quantity and value from those which had existed in the preceding period.

Although the U. S. Department of Commerce has already established commercial agencies and appointed experts in numerous countries for the purpose of supplying information to manufacturers and traders, these efforts are still to be intensified[1]), a

[1]) *Chem. Industrie* **37** (1914) 93.

proposal having been laid before the House of Representatives with the object of proceeding much more energetically in this direction in the future. It is a significant fact that the reason given for advocating this increased activity is the success of similar efforts on the part of the German experts in countries overseas, and especially in South America, these successes having inspired feelings of uneasiness in Government circles in the United States. These demonstrations and activities in the United States naturally make it appear all the more urgent to continue to improve the German organizations for the extension of German export Trade, in which the German chemical industry is greatly interested. These organizations are certainly capable of improvement in many directions.

The exports of merchandise from the U. S. Consular district of Leipzig in the year 1913 show the very serious decrease of not less than $ 834161.—. On the other hand, the value of exports of essential oils has risen from $ 363046.— in the year 1912 to $ 452621.— last year.

Unfortunately no change for the better has taken place in the vexatious position of affairs in Mexico, and in view of the contradictory reports of the prospects which reach Europe, it is best to express no opinion whatever. It is to be regretted that the United States have not seen their way to put an end to the disorders, for it is obvious that their interests are most of all jeopardized by the continuance of chaos. Here the grave consequences resulting from the Monroe-doctrine are once more plainly shown, seeing that it is certain that order could have been restored long ago by joint action by the European Great Powers were it possible for them to interfere. It is true that it is claimed on the part of Mexicans that the existing conditions are often exaggerated in the European press, but even if we merely take as a guide the facts which are confirmed from the other side, it must be admitted that the situation is desperate and that it is scarcely possible to exaggerate it.

With regard to the situation in Brazil we take the following particulars from the report of the *Deutsche Überseeische Bank*. They embrace everything that is of interest as bearing upon this important selling market: —

The economic life of Brazil (the report states) which had made such brilliant progress in the course of recent years, has suffered serious disturbances in the year under review, leading to an acute crisis in almost all branches of commerce. For the first time for many years the statistics show an excess of imports over exports, as will be seen from the figures below: —

	Exports	Imports
in the year 1913	£ 64612292	£ 67169929
„ „ „ 1912	£ 74649143	£ 63424637.

It should be remembered that in 1913 coffee, the principal product of Brazil, alone accounted for about 70 p.c. of the total exports, that is to say about 10 p.c. more than in each of the two preceding years, when its share amounted to about 60 p.c. only. Hence the pronounced and unexpected drop in coffee prices which, after great fluctuations, reduced the quotation for the standard Type (No. 4) at Santos

from Rs. 7 $ 700 per 10 kg. on 1st January, 1913,
to „ 5 $ 400 „ 10 „ „ 31st December, 1913,

has been of the most far-reaching importance, and has inflicted the gravest injury upon the economic conditions of the coffee-growing Central States, especially the State of São Paulo. There is at present very little prospect of any improvement in the miserable condition of the northern States of Pará and Amazonas, which depend

almost entirely upon the course of the rubber market. Owing to the increasing output of the Eastern plantations the average price of rubber stood at

	Rs. 4	$ 342	per kg.	in	the	year	1913
against	„ 5	$ 709	„	„	„	„	„	1912
and	„ 6	$ 195	„	„	„	„	„	1911.

The result of this competition has been something like the commercial annihilation of Pará-rubber, in spite of its admittedly superior quality. It remains to be seen to what extent the measures taken by the Brazilian Government with the object of reducing the costs of production will be successful. So far the conditions in the State of Rio Grande do Sul have worn a more cheerful aspect, because this agricultural district again derived very satisfactory profits from its extensive trade in skins and its dried-meat industry. Favourable prospects for the country are also held out by the attempts to open up the rich iron-deposits in the State of Minas Geraes, which are apparently progressing by private bargain. The money-market was not only deprived of the stimulant of the liberal supply of European capital which it had enjoyed in past years, but as a result of the complete displacement of the commercial and financial balance of the country, which involved the need for making remittances to foreign countries, considerable sums were withdrawn from it. In the place of the old readiness to give credit and strongly-marked optimism, which have often led to an over-hasty and ill-founded extension of national commerce and industry, there appeared a general reserve and feeling of insecurity, made more acute by the scarcity of money in Europe, and this brought about an extraordinary strain upon the finances, to which numerous economic enterprises fell victims.

Although the year 1913 has been in many respects a year of continued favourable development for the Argentine Republic, it must nevertheless be described as a positively critical one for Argentine commerce. Suspensions of payment have assumed astounding dimensions, business has been neglected, and it has been difficult to collect outstanding debts. According to a report of the German Consul General at Buenos Ayres the suspensions of payment in the last four years represented the following totals in Millions of Pesos (Paper).

1910	1911	1912	1913
44,4	63,4	82,4	**172,9.**

The causes of this striking increase in the bankruptcy statistics are said to be very closely connected with the accumulation of large stocks of merchandise, speculation in real estate, and the conditions of the European money-market. The price of land was driven up by speculation to figures far in excess of the intrinsic value of the plots. Things went well so long as foreign capital flowed into the country and the banks accorded credit freely. But the influx of foreign capital was suddenly converted into withdrawal and the banks found themselves compelled to restrict their credits to the utmost. Speculation in real estate came to an end at a single stroke and the liabilities which had been assumed could not be fulfilled. Corresponding to the recent great development of economic enterprises of all kinds in the Argentine, the extent of the financial distress is far greater on the present occasion than in previous years of business-crisis. Even large commercial houses, considered to be securely established, are tottering. The reflex-action of the convulsion extends as far as Europe. Nevertheless there is no cause for anxiety concerning the future of the country. Agriculture and cattle-raising are in a healthy condition and are generally continuing their thriving development. The times of commercial stress through which the country is now

unquestionably passing will free it from all manner of unwholesome excrescences of excessive speculation. Whenever the tension in the European money-market relaxes and good crops bring fresh supplies of cash into the country, the good times will return in the Argentine. Fortunately, thanks to the caution exercised by our representatives, we have escaped from the crisis without losses.

By Law No. 8930 of 27th September 1912 [1]) and the Decree of 10th December 1912, embodying the regulations under which the law is to be carried out, the old fixed tax on perfumeries, toilet-requisites and medicinal specialities was abolished, and replaced by a graduated scale of taxation, based upon the retail selling-price of the article. Each bottle of scent was to bear an adhesive stamp corresponding in value to its retail price. As a result of the objections made by the traders affected to this form of levying the impost, the Government decreed on 14th February 1913 that a tariff for the assessment of the tax should be drawn up by a special commission, and suspended the application of the sections of the law relating to this matter until this commission had reported, or for a period of 6 months, whichever term was the shorter. The period of grace expired before the tariff had been drawn up, and by decree of 21st August 1913 the Government prolonged the term by a further 3 months. This second period has also come to an end without the tariff having been prepared. In the meantime the Government has laid before the Legislature a Bill which is intended, when passed, to take the place of Law No. 8930, and on 15th November 1913 a further decree was promulgated under which the regulations now in force will remain valid until the new law has been passed. The graduated tax calculated upon the retail selling price has thus been put off until further notice.

Uruguay, like its neighbour Argentina, has passed through a crisis last year, mainly brought about by the unsatisfactory state of credit, but speaking generally the country has made satisfactory progress. In a recent speech on the occasion of the opening of the new Legislative Session the President expressed a favourable view of the present situation and prospects of the Republic. He said: "The financial year 1913/14 will close under conditions of complete order and with a surplus of revenue. Internal and external credit is firmly established, so likewise is the value of real estate. The imports amounted in value to 240, the exports to 315 million francs, a balance in favour of the country of 75 million francs. The harvest and the wool-clip promise good results and an improvement in the economic condition is therefore to be expected."

The situation in Chile, according to the report of the *Deutsche Überseeische Bank*, has suffered last year from a depression in tone which was felt throughout commerce, but especially in the import-trade. Even the comparatively favourable development of the nitrate of soda and copper industries and the satisfactory result of the harvest, which is described as a fair average, were unable to modify this depression to any material extent.

The exports of the two products which are of the greatest importance for Chile have shown an increase last year; in the case of nitrate of soda a very considerable one, namely over 5 000 000 cwts. Spanish. On the other hand, the movement of prices of both articles was rather irregular and often downwards. In regard to nitrate of soda it is to be noticed that the manufacture of artificial manures is beginning to acquire more and more importance, and it is to be hoped that the great expansion of consumption will effect a certain compensation, and will prevent a slump in the nitrate-market.

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[1]) *Report* October **1913**, 17.

The exports of nitrate of soda were as follows: 59 306 648 cwts. Spanish in 1913 (1 cwt. Spanish = 46 kilos) compared with 54 199 439 cwts. Spanish in 1912, while the copper shipments amounted to 887 895 cwts. Spanish in 1913 compared with 823 970 cwts. Spanish in 1912.

The total value of the exports and imports in the two last years for which records are available (the figures for 1913 have not yet been published), were as follows: —

	Exports	Imports
in the year 1912 Chil. Gold $ (at 18 d.)	383 227 949	334 454 779
„ „ „ 1911 „ „ „	339 409 350	348 990 300.

The causes of the depression in trade referred to above should probably be sought not so much in the reaction of conditions prevailing in Europe, as in those of the country itself, in particular in the steady fall of the rate of exchange (the rate for 90 days' bills on London declined in the course of the year from $10^3/_8$ d. to $9^1/_8$ d.) and the increasing cost of living connected therewith.

The Chilian Government is endeavouring to bring about an improvement in the situation, and with this end in view has laid a Bill before Congress for the establishment of a conversion-fund, which besides converting the paper currency at a rate of exchange still to be determined, between 10 and 12 d., is to furnish to the economic life of the country a certain mobility in the means of monetary circulation. Whether these intentions will be realized still appears to be questionable, for there are not lacking in Chile influential voices which declare the carrying-out of these measures under the present conditions to be inappropriate. The Government already has at its disposal the gold required for the contemplated conversion, a fund of 160 million marks, deposited abroad, being available to redeem the paper currency, representing about 150 million pesos, now in circulation.

In Peru affairs do not seem inclined to take a turn for the better. The country is suffering seriously from scarcity of money and from the low prices of rubber and sugar.

In the Far East, the chief interest, as before, continues to be centred in Japan. The state of trade in that country may be described as unchanged, and during the year 1913 no exceptional events have signalized Japanese commerce. Progress has been undisturbed and a considerable increase both in imports and exports has to be reported. The values were as follows: —

	1912	1913
Imports . . .	618 992 277 Yen	729 431 644 Yen
Exports . . .	526 981 842 „	632 460 213 „ .

These statistics do not include the commercial figures for Korea and Formosa. The record-value for the entire trade of the country, that of 1912 (when the turnover for the first time exceeded 1000 millions yen), has therefore been surpassed, and that in a considerable measure, by last year's results[1]). For Old Japan alone the value of the imports in the closing days was given as 19,5, and that of the exports as 23,4, total trade 42,8 million Yen. On the basis of these returns, therefore, the figures for Old Japan for the entire year would be as follows: —

Imports	705 997 000 Yen
Exports	610 723 000 „
Total trade	1 316 720 000 „
Excess of imports	95 274 000 „ .

Trade with the different parts of the world, compared with that of 1912, showed the following results: —

	Exports	Imports		Exports	Imports
Asia .	+ 28,4 %	+ 34 %	America . .	+ 8,1 %	+ 5 %
Europe	+ 28,1 %	+ 7 %	Other parts	+ 1 %	+ 14 %.

It follows from these figures that the largest absolute increase in the imports of Japan has been from Asiatic countries, Asia, moreover, being the only part of the world of which the increase in imports to Japan has been greater than the increase in exports from that country. Therefore, both in respect of imports and exports, Asia still occupies the first position in Japanese commerce. Europe comes next, and has outpaced America as a market for the sale of Japanese produce, America now taking third place.

The table below shows the increases and decreases (in million of Yen) of the principal articles of export and import: —

Exports		Imports	
Raw silk	+ 35,66	Raw cotton	+ 30,75
Cotton yarn	+ 17,82	Sugar	+ 20,4
Cotton goods	+ 8,2	Rice	+ 17,28
Habutage	+ 7,32	Oil cakes	+ 11,76
Coal	+ 3,07	Wheat	+ 7,99
Copper	+ 2,72	Machinery	+ 5,59
Wood	+ 2,2	Woollen goods	+ 3,57
Woven goods	+ 1,6	Pig iron	+ 30,04
Porcelain	+ 1,14	Hemp	+ 2,79
Fish oil	+ 1,25	Iron tubes, &c.	+ 1,85
Tea	— 3,35	Rails and iron sheets	— 2,95
Straw plait	— 0,6	Nails	— 2,09
Camphor	— 0,61	Petroleum	— 1,22
		Wool	— 1,3
		Skins and Hides	— 0,09
		Grey shirtings, Printed cottons	— 0,76

The press of Japan is very satisfied with the results of last year's trade. It is pleased with the "record" figures shown, and especially with the fact that these have been achieved in spite of many untoward events. Among these are included the constitutional struggle in the spring, the Balkan troubles and the tightness of money in Europe, the repeated fall in the rate of exchange of silver, the entanglements of Japan with California, the strike of weavers in the United States, the banking-difficulties with India, and, foremost of all, the revolutionary struggle in China. A few papers again indulge in lamentations over the increase in the excess of imports; the Government organ, *"Chuo"*, however, consoles them with justice with the reflection that in spite of these complaints, which are heard afresh every year, the commercial turnover increases annually. This paper also stigmatizes as absurd the statement which would connect the excess of imports over exports with the dwindling of the cash-reserve in London. So far as the excess of imports over exports (called "the passive commercial balance") is concerned, it cannot be said until detailed figures are available what are the figures

[1]) *Ostasiatischer Lloyd* **1914**, No. 3.

pertaining to each particular group of commodities and how much of the imports is consumed within the country itself. A notable article has appeared in the economic review *"Keizai Yasshi"*, in which it is declared that the future of Japan lies in the textile industry, beside which the chemical-, engineering- and other industries only offer insignificant prospects. This paper recommends the gradual abolition of all protective duties and of the taxes on trade, together with the gradual transfer of the exports of cotton yarn and raw silk to exports of finished cotton and silk fabrics.

The rice-crop, of which the result is of paramount importance for the whole economic life of Japan has, according to a report by the Ministry for Agriculture and Commerce, dated 4th February 1914, afforded a yield in Old Japan of 50 229 935 koku, equalling about 90,6 million hectolitres. The result of the crop was therefore almost the same as in the foregoing year, and only exceeded by very little the so-called average yield, which is estimated by Japanese statisticians from the yields of the preceding 7 years, leaving out of account the most and least favourable years (in the present case the years 1909 and 1905) and is given as 49 910 855 koku.

As in previous years, the result of the crop has again fallen much below the official estimates, which were at first 52,8 and afterwards 51,3 million koku. These estimates are usually tinged with great optimism.

The Japanese soap-industry, which is the most important of all so far as concerns the consumption of our manufactures, is able to look back upon a satisfactory year. When the disturbances in China had quieted down, large orders were again received from that country, and in Manchuria also business revived. Recently Japan has also taken up the export of soap to the South Sea Islands, and the future development of this industry therefore warrants the highest hopes.

The exports of toilet soap from Japan[1]) in 1913 amounted to $ 750 997, which is $ 533 338 more than was exported in 1912. Laundry soap does not show a large volume, but the increase is noteworthy. Below are the figures: —

Articles	1912	1913
Toilet soap . . .	$ 217 659	$ 750 997
Laundry soap . .	„ 4,628	„ 7 807
Total	$ 222 287	$ 758 804.

The centres of the soap industry are Tokyo and Osaka, the annual output amounting to over $ 2 000 000.

The report of the Hamburg Chamber of Commerce contains the following statement on the business-position in China: —

During the year 1913 China was afflicted by a second revolution which broke out against the provisional President of the Republic Yuan Shi-kai, in the month of July. Yuan Shi-kai was successful in overthrowing the revolt within a comparatively short time, but only by using considerable force. Since then, having in the meantime been fully-elected President, he is busily engaged in strengthening his position. The dissolution of the revolutionary party, the Kuo Ming Tang, decreed by him, and including the dismissal of all the members of Parliament, has proceeded up to the present without any fresh disturbance of the peace. More far-seeing circles in China appear to be gradually adopting the view that vigorous support of the actual President offers the only security for a return of ordered conditions, which the people are genuinely eager to see re-established. The country continues to suffer, and since the second

[1]) *Daily Consular and Trade Reports* **1914**, No. 84.

revolution in an increased measure, of the widespread excesses of robber-bands, recruited from ex-revolutionaries, disbanded soldiers, &c. The most important questions which confront the country, next to the re-establishment of internal order, are those of the Constitution and of Financial Reform and both of these are still unsolved. The Constitutional problem could not be advanced under the sterile Parliamentary régime which was recently prevalent. Since, after endless difficulties, the first great loan of 25 million £ sterling, advanced by the group of the Five Powers, was concluded in the spring of last year, negotiations have been set on foot for a another large loan, but so far as is known they have made no great progress up to the present. In the meantime the Five-Power group continues to exist only for the purpose of concluding large loans, and all the previous international combinations of different groups of banks, with the object of promoting industrial development, railways, &c., were dissolved a few months ago.

The question of the introduction of ordered conditions of currency, which is becoming more and more acute as the foreign trade of China increases, has been pushed into the background again by the political questions that have obtruded themselves. But that it has not been lost sight of altogether, is shown by the appointment last September of a German expert in banking affairs whose duty, in addition to the reconstruction of the Chinese National Bank, it will be to examine the currency-question and to take in hand the preliminary work for the introduction of a programme of reform.

In spite of all adverse circumstances, the import-trade into China began to expand during the first half of the year; but as a result of the July-revolution and its consequences the consumption of the accumulating stocks was seriously arrested, and new orders are therefore coming in slowly. Consumption is further made more difficult by the greatly depreciated paper-money which is still in circulation in some provinces, and for the calling-in of which the Government is at present lacking funds. The almost total cessation of the imports of European apparel is worthy of note: owing to the cost and discomfort in wear European clothing has not proved suitable for the Chinese.

The export-trade from China has continued to exhibit great possibilities of development, but it has been much hampered by disturbances, interruptions of transport from the interior owing to the movements of troops, the depredations of robbers, &c. Exports from Tientsin have again shown an increase, which has been greatly assisted by the extension of railways. In the South-western part of the country continuous rains and the overflowing of the Western River have caused great damage to life and property, the rice-crop in particular has been largely destroyed and the distress of the population caused thereby, together with the general scarcity of money, have greatly hampered export trade in this quarter.

Commercial Notes and Scientific Information on Essential Oils.

Almond Oil, bitter. Since the almost universal admission of synthetic chlorine-free bitter almond oil in the manufacture of comestibles, the genuine oil has been rather neglected, especially because for some considerable time there has been no scarcity of apricot kernels, which constitute the sole raw material of the article. To this must be added the fact that adulteration is more than ever the order of the day, and that the "elasticity" of this article of confidence is being exploited to such an extent by certain firms that so-called "genuine bitter almond oil" may be bought at almost any price, with a "guarantee of absolute purity". The extent of the deception which is being practised in this matter can only be fully judged by those who, like ourselves, are themselves manufacturers of the article, and in spite of assurances to the contrary, most of the pretended manufacturers are not really so. In natural almond oil the hydrocyanic acid-content affords to some degree a means of estimating the absence of artificial additions, but in bitter almond oil free from hydrocyanic acid this factor is absent, and the buyer is completely dependent upon the rectitude of his supplier. Under the influence of the dragging sale we have somewhat reduced our prices.

As V. R. Krieble[1]) pointed out some time ago, when emulsin is allowed to act with amygdalin, l-mandelic nitrile is sometimes formed, while benzaldehyde and hydrocyanic acid in the presence of emulsin may give rise to *d*-mandelic nitrile. In explanation of this phenomenon, Krieble assumes the presence in emulsin of varying quantities of oxynitrilase, the proportions of which are dependent on the presence of *d*- or *l*-mandelic nitrile. As *d*-mandelic nitrile is a component of prunasine and of amygdaline, whereas sambunigrine contains *l*-mandelic nitrile, it was to be expected that in plants which count these glucosides among their constituents, the corresponding *d*- or *l*-oxynitrilase would also occur. In order to elucidate this problem, Krieble[2]) examined the bark and the leaves of the wild cherry, as well as the leaves of the peach, and in these organs did in fact find an enzyme under the influence of which benzaldehyde and hydrocyanic acid afforded *d*-mandelic acid. In elder leaves, however, which contain sambunigrin, he was unable to detect *l*-oxynitrilase. In Krieble's opinion it is not impossible that the last-named leaves may contain equal proportions of *d*- and *l*-oxynitrilase.

G. Bertrand and A. Compton[3]) conclude from the results obtained by them in their investigations of the hydrolysis of salicin, that in addition to amygdalinase, vicianinase, sucrase, vicianase, and cellase, the emulsin also contains salicinase. Salicinase in a 3 p.c. solution is capable of completely hydrolysing salicin.

In conclusion it remains to be mentioned that K. Ohta[4]) has prepared emulsin free from albumin; this emulsin resolves amygdalin much more intensely than does the emulsin of commerce. After six months its activity still remained undiminished.

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[1]) *Journ. Americ. chem. Soc.* **34** (1912), 716. — [2]) *Ibidem* **35** (1913), 1643. — [3]) *Compt. rend.* **154** (1912), 1646; **157** (1913), 797. — [4]) *Biochem. Zeitschr.* **58** (1913), 329; *Chem. Zentralbl.* **1914**. I. 901.

Ambrette Seed Oil. Ambrette seed is barely to be had for its weight in gold, so to speak, and the still available parcels are so small that raw material can fairly be said to be completely wanting. It would be most desirable if the West Indies and Java and would take advantage of the present state of the market to lay down new plantations, for it seems hardly possible that the article can again become so completely depreciated as was the case some years ago, provided of course that certain limitations be observed in the production. Our stock of oil is for the present exhausted.

In our *Report* of April **1912** (p. 25) we enumerated the constants of two samples of liquid ambrette seed oil. Since then we have tested a further series of liquid oils of our own manufacture, of which the limits of value ascertained are recorded below: $d_{15°}$ 0,9088 to 0,9161, α_D + 1° 19′ to — 2° 24′, $n_{D20°}$ 1,47421 to 1,48013, acid v. 0,8 to 2,4, ester v. 137,7 to 180,5, soluble in 2,5 to 6 vols. a. m. of 80 p. c. alcohol. In the case of one sample showing an ester value of 167,4, the ester value after acetylation was found to be 199,7.

In one instance the characters showed a certain degree of deviation from the normal: $d_{15°}$ 0,9298, α_D — 1° 34′, $n_{D20°}$ 1,48519, acid v. 0,7, ester v. 139,8; this sample did not even make a clear solution with 10 vols. of 80 p. c. alcohol, sol. in 0,5 vols. a. m. of 90 p. c. alcohol. In this case the odour also left something to be desired.

Angelica Oil. As was to be expected, the plantations in Thuringia as well as our own angelica-fields in the neighbourhood of our works have furnished a plentiful supply, and it was possible to buy raw material for distilling at exceptionally cheap prices. Although, as might be expected, the essential oil industry supplied its requirements freely, the farmers were unable to dispose of their surplus root, with the result that even at the present time a few remaining lots have been offered in vain at unprecedently low rates. Naturally, the growers in Thuringia have been greatly disappointed by the poor figures realized by their merchandise, and they have decided to abandon the cultivation to a large extent. It is therefore not impossible that the prices of angelica root oil, which are at present low, may advance in the course of the summer. In any case, the present favourable quotations should be an incentive to lay in a plentiful stock.

Angelica seed oil has been offered from France at about 250.— *frs.* per kilo, but very little interest has been shown in the article, because this price of course bears no proper relation to that of the oil from the root. So far as we are concerned, the demand for angelica seed oil has almost ceased to exist, and we were therefore unable to make up our minds to pay the price mentioned.

Anise Oil, Russian. According to the report of our informants, the Russian anise-season of 1913/14 opened on 13th September last. At its commencement the stock, both of seed and of oil, was utterly exhausted, as the United States, in anticipation of the impending increase in Customs Duty, had cleared the remaining balance off the market as early as the months of April and May. The total arrivals at the two principal markets in Krasnoia and Alexejevka amounted to 1 300 000 kilos, and the small arrivals at markets other than these to about 400 000 kilos, a grand total of 1 700 000 kilos. As our informants have ascertained that at the present time no stocks whatever are left in the hands of the farmers, the above quantity may also be taken to represent the total output of the crop of 1913. The yield, therefore, is one which must be designated

as "below the average". Since the beginning of the season the export trade has dragged, partly because for the reason stated above the United States still held large stocks, secondly because the consumers on the coasts of the Mediterranean were able to supply themselves with Bulgarian seed, and thirdly because all the users only bought as much as they absolutely needed, owing to the defective quality and the high price. Up to the beginning of March only about 800 000 kilos had been exported and therefore, estimating the requirements of the Russian anise-oil distillers for the current year at about 300 000 kilos, which appears to us to be a very low estimate, about 600 000 kilos would still be available in second-hands, of which no doubt the greater part will go into consumption between now and the arrival of the new crop to meet current requirements. With regard to the quality of the anise-seed of the 1913 crop it is to be noted that the first sowings suffered greatly from drought and, as a result, gave a poor yield of dark-coloured seed, while the second sowings yielded a medium output of green-coloured seed, which, however, in many cases was not completely matured. As, in bulking the seed, the green quality was not usually kept separate, the average quality was of unequal appearance. Foreign matter, especially coriander seed, was over-plentiful. The average oil-content of the 1913 anise is thoroughly unsatisfactory, amounting only to 2,2 p. c. of crude oil with an anethol-content of from 70 to 75 p. c. This inferior oil-yield is said to be due, in part, to the defective state of purity of the seed, for the higher the price, the more the seed which is brought to market is mixed with impurities.

From the statistics it would appear that the cultivation of anise in the Government of Voronesh has declined. The rising value of land, the increased wages, and the troublesome nature of the crop, together with the poor yields of the last few years, are causing the farmers to turn their attention to other products which are easier to grow and more remunerative.

It goes without saying that in view of the conditions depicted above, the prices of Russian anise oil were high, and that the future of the market does not hold out any prospects in favour of the consumer. The demand for our superior quality with a solidifying point of 18° has throughout been exceedingly strong, and our stock is therefore at present inconsiderable.

Oil of Artemisia vulgaris, Chinese. At the Imperial Institute in London[1]) an oil-sample received from Hong-Kong under the name of *"Ngai Yau"* has been examined. It was probably the product of common mugwort (*Artemisia vulgaris,* L.). Its characters were as follow: $d_{15°}$ 0,9390, sap. v. 103,3, sap. v. after acet. 205,87, sol. in its own vol. of 90 p. c. alcohol; when more alcohol was added the mixture turned turbid.

The oil differs in respect of density and saponification value from the oil of Indian *Artemisia vulgaris* which we examined last year[2]).

The U. S. Consul at Hongkong[3]) also reports on Chinese oil of *Artemisia vulgaris,* an article which is of local commercial importance. Its principal use is in medicine; it is given internally, drops of it being added to the tea, as a remedy for colds and similar complaints, and also externally in the form of a liniment in rheumatism and such-like affections. The oil is sold by the Chinese in small bottles as a patent medicine. At present the wholesale trade price is $ 400.— local currency per picul = about $ 1.45 gold, per lb.

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[1]) *Bull. Imp. Inst.* **11** (1913), 436. — [2]) *Report* April **1913**, 28. — [3]) *Daily Cons. and Trade Rep.*, Washington **17** (1914), No. 56, p. 906.

Oil of Sweet Basil. This article, which used to be so popular, has remained in the condition of total neglect of which it has now suffered for many years. Sooner or later it may disappear from commerce altogether.

On account of its origin mention may here be made of an oil of sweet basil produced in Central Africa. The oil was of a yellow colour, it possessed the aroma characteristic of oil of sweet basil and its constants harmonised with those of the distillate produced in Europe, (France, Germany and Spain), and in Algeria: $d_{15°}$ 0,9185, α_D — 8° 10′, $n_{D20°}$ 1,48490, acid v. 1,1, ester v. 6,4, sol. in 4 vols. a. m. of 70 p. c. alcohol, and in 1 vol. of 80 p. c. alcohol a. m.

Bay Oil. There has been no lack of sufficient supplies during the last few months, and it has therefore been possible to reduce the price. Besides the exquisite West Indian qualities, however, parcels of bay oil were imported occasionally which had been adulterated with oil of cloves and pimento to a degree which made identification almost impossible. As we have ascertained that these parcels have found buyers in the European market, we would warn the trade against allowing the price to be the principal guide to buying. By using such oil as described above many a bay-rum manufacturer has already lost his reputation and his customers. Our terpeneless bay oil continues to enjoy the keenest possible demand, and is particularly useful for manufacturers to whom the limited solubility of the natural bay oil offers an obstacle in the making of their preparations.

Betel Oil. H. H. Mann, D. L. Sahasrabuddhe and V. G. Patwardhan[1]) have published an investigation into the chemistry and physiology of betel leaves. In addition to various reducing and non-reducing sugars, the leaves contain starch, tannin and diastases, as well as from 0,8 to 1,8 p.c. essential oil, the younger leaves being the richest in oil. The leaves are bleached in the months of August, September and October. The moistened leaves are kept in a warm, well-aired, shady place. After an interval of about 8 days the leaves that are already bleached are picked out, and the rest is left lying. About one-half of the leaves rot under this treatment. In the unbleached leaves the percentage of volatile oil remains constant, but in the bleached leaves the proportion of oil increases considerably, namely from 1,2 to 4,2 p. c. The bleaching-process is due to oxidation and only takes place in the presence of acids; the leaves themselves and the essential oil are almost completely destroyed by traces of alkali.

Birch Bud Oil. It is well known that the high paraffin-content of this oil greatly impedes its solubility, and it is therefore not surprising that our readily-soluble birch bud oil, which is miscible with 80 p.c. alcohol in any proportion, is almost everywhere preferred. The difference in price is more than compensated by the advantages in use which this oil possesses.

Buchu Leaf Oil. Our scanty supplies have been quite sufficient to cover the feeble demand. The price of buchu leaves has remained high, and we therefore intend to sell the whole of our stock of oil before laying in new supplies of raw material.

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[1]) *Mem. Dep. Agric. India, Chem. Series* **3** (1913), 17; *Journ. Soc. chem. Ind.* **32** (1913), 922.

G. R. von Wielligh[1]) reports on the history, cultivation, and commerce of the buchu shrub in South Africa. Instead of cultivating the plant, it has in many parts been cut down or uprooted. The result of this has been that the plants are now only found here and there in small numbers, so that it scarcely pays to collect the leaves. It does not, however, appear to be very easy to cultivate the buchu-shrub, for the cuttings take root with difficulty; they thrive best in very sandy soil. The reason may also be that so far there is little experience to go upon in the matter of systematic cultivation, as the buchu-shrub is only occasionally grown as an ornamental plant.

Possibly this state of things may undergo a change now that the Bill to which we referred on p. 28 of our last *Report* has been passed into law.

Cajuput Oil. The value of this article has undergone no changes whatever during the last few months. The arrivals were sufficient to satisfy the requirements, especially because a small stock still remained on hand from the year 1912. As previously, the largest quantities again went to the United States, where the oil is used in the manufacture of a few well-established patent medicines. In Europe, the cheaper grades of eucalyptus oil constitute dangerous competitors for cajuput oil. No statistical details are available on the present occasion; since the official export-lists of Macassar have ceased to enumerate cajuput oil independently it is difficult to obtain accurate information concerning the shipments.

We gather from the *American Perfumer*[2]) that the Bureau of Chemistry of the Department of Agriculture of the United States has rejected, among other oils, a sample of cajuput oil because it contained copper. On this we would observe that a slight copper-content is almost characteristic of crude cajuput oil, and in the vast majority of cases is the agent to which its green or bluish-green colour is due. The presence of copper is therefore simply an indication that the oil is in the crude state, but does not warrant any conclusion as to the oil being adulterated or otherwise. Seeing that the United States Pharmacopœia lays it down that cajuput oil shall not give a reaction for copper, the sample referred to above should only have been rejected on the ground that it did not conform with the requirements of the U. S. Pharmacopœia.

Calamus Oil. The scarcity of this article, of which we have already had to complain in our last two *Reports*, still continues, for the small quantities of calamus root which are gathered in the low-lying grounds of the central Elbe and the Saale rivers are quite insufficient to supply enough oil to cover the requirements even approximately. Russian calamus root is either wanting altogether, or is being offered at prices which leave no profit even at the present high quotations of calamus oil. It is true that some interest has been shown on the European markets for a few small parcels of Japanese calamus oil, but the quality of these was too abnormal to make them suitable as a substitute for the usual European oil.

How popular an adulterant glycerol acetate has become is evident from the fact that we found it to be present in a sample of calamus oil recently submitted to us for our opinion; that is to say, in yet another oil of which the value does not at all

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[1]) *Agricultural Journal of the Union of South Africa*, July 1913; *Chemist and Druggist* **83** (1913), 403. Also comp. *Oil, Paint and Drug Reporter* **84** (1913), No. 18, p. 35. — [2]) *Americ. Perfumer* **8** (1913), 225.

depend upon the ester-content. Generally speaking the properties of the sample agreed with those of a normal oil, except that ester-value was too high: $d_{15°}$ 0,9628, α_D + 11° 52′, acid v. 0,9, ester v. 89,4, soluble in any proportion of 90 p.c. alcohol.

The ester value of normal calamus oil ranges from 6 to 20, hence the suspicion at once arose that an artificial ester had been added to the sample under examination. It is true that the first test which was applied, that for terpinyl acetate and the esters of sparingly-soluble acids, was without result, but the presence of glycerol ester was established. Extraction with 5 p.c. alcohol resulted in the removal of 5 p.c. of glycerol acetate with the following constants: b. p. 114 to 116° (3 mm.), $d_{15°}$ 1,1677, acid v. 0,6, ester v. 737,8. From these constants it was to be inferred that the substance consisted chiefly of triacetine. For the purposes of further identification the ester was split up into its constituents, when the glycerol was identified by the acroleine-reaction and the acetic acid by conversion into acetic ester. In the course of further examination it was shown that by no means the whole of the glycerol ester in the calamus oil had been taken up by the 5 p.c. alcohol, for when the extracted oil was fractionally distilled, further considerable quantities of glycerol ester were isolated. The total addition was estimated at probably about 10 p.c., a percentage which would also correspond with the ester value of the sample.

The fact that the oil possessed a subsidiary odour of caraway induced us to treat it with a 40 p.c. sodium sulphite solution. By this manipulation we succeeded in isolating a certain proportion of carvone, which was identified from the oxime. Unfortunately we obtained only such a small quantity of this oxime that is was impossible to recrystallise it; and it was therefore necessary to determine the m. p. from the crude product. It was 69° instead of 72°. We have convinced ourselves that carvone is not a constituent of pure calamus oil. But as the sample under examination only contained traces of carvone we cannot ascribe its presence in this case to adulteration, but only to contamination.

It is true that no other foreign bodies could be detected in the sample, yet the specific gravity of the oil, after the extraction with 5 p.c. alcohol, was much too low to enable us to class it as a normal calamus oil. We therefore suspect that it consisted of a by-product in the manufacture of terpeneless calamus oil, mixed with glycerol acetate.

In a sample of oil distilled from Russian calamus root grown in the Baltic provinces, F. W. Semmler and K. E. Spornitz[1]) have found several constituents not previously encountered in this oil. The low-boiling portions (b. p. 45 to 50°, 9 mm.; α_D + 59°) contained α-pinene, which was identified by converting it into the nitrosochloride (m. p. 108°). An earlier examination by A. Kurbatov[2]) had already pointed to the probability of the presence of this terpene. Kurbatov found the oil to contain 5 p.c. of a hydrocarbon with b. p. 158 to 159°, which yielded a hydrochloride with an exceptionally low m. p. (63°). In addition to pinene, the authors succeeded in identifying camphene by conversion into *iso*borneol (m. p. 212°). Another fraction (b. p. not stated) contained camphor (m. p. of the oxime 115°). A fraction with b. p. 130 to 135° (12 mm.), after being boiled over sodium, afforded a sesquiterpene $C_{15}H_{24}$, calamene, which possessed the following properties: b. p. 123 to 126° (10,5 mm.), $d_{19°}^{20°}$ 0,9224, α_D + 5°, n_D 1,50572. By treatment with hydrogen in the presence of platinum black

[1]) *Berl. Berichte* **46** (1913), 3700. — [2]) *Berl. Berichte* **6** (1873), 1210. — *Liebigs Annalen* **173** (1874), 4.

two double bonds were saturated, giving rise to tetrahydrocalamene, $C_{15}H_{28}$, b. p. 123 to 125° (10 mm.): $d_{19°}^{20°}$ 0,8951, $\alpha_D \pm 0°$, n_D 1,48480. In the opinion of the authors this fact conclusively proves the bicyclical character of the sesquiterpene, and judging by its density they class it among those which are derivatives of naphthalene. The body could not be reduced with sodium and alcohol, hence the double bonds are not in the conjugated position. No solid hydrochloride was afforded; neither was any result obtained when hydrating by Bertram and Walbaum's method. It was also found impossible to obtain any characteristic decomposition-products from the ozonide.

The authors further obtained a fraction (b. p. 150 to 160° at 13 mm.; $d_{28°}$ 0,9611; n_D 1,5098) of which the analysis pointed to the presence of a substance $C_{15}H_{24}O$. This body appears to be a tertiary alcohol which readily splits off water. Water was invariably eliminated from it, when it was boiled with acetanhydride, or treated with phthalic anhydride or with zinc dust in a sealed tube. When boiled for a short time with concentrated formic acid the body $C_{15}H_{24}O$ affords a hydrocarbon, calamenene, $C_{15}H_{22}$, b. p. 136 to 143° (15 mm.): $d_{19°}^{20°}$ 0,9324, $\alpha_D + 6°$, n_D 1,52317. Complete reduction with hydrogen in the presence of platinum black gave rise to an inactive substance, hexahydrocalamenene, $C_{15}H_{28}$, b. p. 122 to 124° (9 mm.).

As a result of these investigations Semmler and Spornitz regard it as highly improbable that the hydrocarbon $C_{15}H_{22}$ described by Thoms and Beckström[1]) is a natural constituent of calamus oil; they rather suspect it to have been produced by the splitting-off of water from the body $C_{15}H_{24}O$. On the other hand they believe the hydrocarbon $C_{15}H_{24}$ to be a natural constituent of calamus oil, and not a reduction-product of calamenene.

In the course of the examination of a small oil-sample the authors obtained an alcohol-fraction with b. p. 150 to 160° (13 mm.), $d_{20°}$ 0,9688, $\alpha_D + 8°$, n_D 1,51263, which contained a sesquiterpene alcohol $C_{15}H_{24}O$, of which the acetic ester boiled between 155 and 163° (12 mm.).

As will be observed, Semmler and Spornitz have altered the nomenclature, by re-naming the hydrocarbon $C_{15}H_{22}$ from calamene into calamenene and by calling the sesquiterpene $C_{15}H_{24}$, calamene. The body $C_{15}H_{24}O$ they call calamenenol, while they reserve the name calamenol for the alcohol $C_{15}H_{26}O$ which still remains to be found.

H. Thoms and R. Beckström[2]) account for the fact that the outcome of the Semmler-Spornitz research differs in part from their own results by the different origin of the oils. They point out that whereas they examined a terpene-free fraction of a Japanese calamus oil, Semmler and Spornitz, as stated above, experimented with a Russian oil.

Thoms and Beckström do not consider it impossible that the hydrocarbon $C_{15}H_{22}$ may be generated from the body $C_{15}H_{24}O$ by the elimination of water consequent upon the method of treatment (treatment of the fraction in question with concentrated aqueous solution of arsenic acid for the removal of the asarone). But in Semmler's work they can find no proof that under the conditions mentioned by the authors the arsenic acid splits off water from the body $C_{15}H_{24}O$.

Camphor Oil. During the winter the Japanese camphor oil market, considered as a whole, has remained unchanged. Traffic in this important raw material is made

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[1]) *Berl. Berichte* **34** (1901), 1021. — [2]) *Berl. Berichte* **46** (1913), 3946.

very difficult by the practice of the Japanese to dispose of the different grades of the oil only in parcels assorted in definite proportions. If a buyer, for instance, wishes to acquire 1000 cases of white camphor oil, he is obliged to buy at the same time several thousand cases of brown oil, for which, possibly, he may have no use until the distant future. This business custom of the Japanese greatly impedes operations in camphor oil, and it is to be regretted that, as we are informed, there is no prospect of the abolition of the restriction thus forced upon buyers. The call for our light camphor oil has at times been particularly brisk, especially from England, whence during the month of February an exceptionally strong demand manifested itself. It is true that our stock of heavy camphor oil has not been drawn upon to the same extent, but this oil also has gradually become indispensable for many technical purposes. The prices of both qualities have remained unchanged, and the steady sale is likely to keep the values at their present level during the near future.

The local authorities of the District of Tokyo have last year initiated experiments on a large scale in planting camphor trees on the island-groups situated in the Bay of Tokyo, and especially on the large volcanic Island of Oshima and on the Hachijojima-group, north of the Bonin Islands[1]). The trees have stood the summer well, and are said to be making rapid growth. As a result, neighbouring local authorities have followed the example of Tokyo, and afforestation with camphor trees is at present being carried out on the islands near Idzu and on the Bonin Islands[2]). At the beginning of November the first experiment in camphor-refining was also made at Oshima, and if the experiments should be successful, the Tokyo local authorities intend to lease the exploitation of camphor on their islands to private companies. In the Island of Formosa, the principal centre of production of Japanese camphor, the last business year has been a very good one. In 1911 the Monopoly Bureau's exports reached a total of 5,7 million lbs., of a value of 3,6 million *Yen,* but in 1912 the figures were 8,7 million lbs., of a value of 5,6 million *Yen.* The principal buyers were the United States and Germany, each of which took about 2,3 million lbs.; Old Japan took 1,7 and England 1 million lbs., France about 900 000 lbs. and India 300 000 lbs. For the current year the figures for America and Germany are pretty much the same, England and France have taken considerably increased quantities, and the Indian takings have trebled. But the greatest increase of all is with Old Japan which, it is true, re-exports in turn to other countries, but whose own camphor industry is nevertheless the principal factor accounting for these increased imports. Side by side with the increase in exports there was a reduction in the output in Formosa, with the result that the stocks there are now pretty nearly exhausted. For this reason the management of the Monopoly is now engaged in devising measures for accumulating a sufficiency of fresh supplies as soon as possible. The result of the experiments in the preparation of camphor from leaves has shown that the quantity of camphor contained in the leaves of the tree equals about 25 p.c. of that which is obtainable from the trunk, branches, and twigs. To the question whether enough camphor trees are being planted to compensate for those that are cut down, the Monopoly authorities return a distinct affirmative. It is said that in the districts inhabited by the subdued aborigines large areas of camphor-trees have also been found to exist, and that there is consequently no cause for anxiety as to the future production of camphor.

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[1]) *Ostasiatischer Lloyd* **1913**, 50. — [2]) Comp. *Report* April **1913**, 38.

From an official Japanese publication[1]) we take the following statistics respecting the production in Japan and exportation from that country, of camphor and camphor oil:—

PRODUCTION OF CAMPHOR AND CAMPHOR OIL IN JAPAN.

YEAR	STATIONS	CAMPHOR		CAMPHOR OIL		TOTAL VALUE
		Kin	Yen	Kin	Yen	Yen
1902[2])	1299	2 549 556	1 841 910	789 453	158 052	1 999 962
1903	1219	2 211 438	1 828 953	432 820	129 826	1 958 779
1904	1717	638 796	330 043	714 370	202 191	532 234
1905	1564	600 085	329 916	652 556	189 417	519 333
1906	1617	734 625	436 282	850 464	264 847	701 129
1907	1618	746 729	474 605	959 316	316 356	790 961
1908	1793	826 367	517 723	1 023 903	333 756	851 479
1909	1931	832 271	461 218	1 143 454	328 741	789 959
1910	2615	1 054 343	587 040	1 663 324	477 350	1 064 390
1911	2934	1 103 058	615 757	1 845 403	529 552	1 145 309

The exports of camphor from Japan in the last 10 years were as follows:—

	Yen		Yen		Yen		Yen
1902	3 404 833	1905	2 566 233	1908	2 063 410	1911	3 143 084
1903	3 537 844	1906	3 632 785	1909	3 469 398	1912	2 826 754
1904	3 168 197	1907	5 026 858	1910	2 964 369		

The value of the camphor exported to different countries in the years 1906 to 1912 inclusive was as follows:—

CAMPHOR EXPORTS FROM JAPAN.

	1906 Yen	1907 Yen	1908 Yen	1909 Yen	1910 Yen	1911 Yen	1912 Yen
Germany	509 521	1 301 544	375 642	545 583	322 430	475 337	435 949
British India . .	656 835	1 069 354	355 903	489 321	477 649	612 832	677 624
France	1 069 641	604 733	301 621	518 516	748 626	668 517	430 650
United Kingdom .	104 298	158 651	147 331	890 413	580 023	592 685	651 086
U. S. of America .	1 217 682	1 689 577	731 004	824 646	691 029	596 955	389 986
Other countries .	74 808	202 999	151 909	191 916	144 612	196 758	241 459
Total	3 632 785	5 026 858	2 063 410	3 469 398	2 964 369	3 143 084	2 826 754

From p. 189 of the said Year Book we take the following statistics relating to the camphor production in Formosa:—

	CAMPHOR Kin	CAMPHOR OIL Kin		CAMPHOR Kin	CAMPHOR OIL Kin
1902	3 148 742	2 388 135	1907	3 914 598	4 180 894
1903	3 595 814	2 678 794	1908	3 534 970	4 446 823
1904	3 540 953	2 805 809	1909	3 537 712	3 870 254
1905	2 865 117	2 373 788	1910	5 360 642	5 858 145
1906	3 252 408	2 986 023	1911	4 509 412	5 306 044

[1]) *Finanz. u. wirtsch. Jahrbuch f. Japan* **13** (1913), 73. — [2]) The figures for the years anterior to 1904 are those relating to the calendar years, from 1905 inclusive they represent the results of the financial years (April 1 — March 31). — [3]) *Finanz. u. wirtsch. Jahrbuch f. Japan* **13** (1913), 102. — [4]) *Ibidem* **13** (1913), 106.

According to an article which has appeared in an English technical journal[1]) the Camphor Monopoly has not come up to expectations and only yields a small profit. In the Budget for 1913/1914 the profit was estimated at not more than 114914 Yen. Compared with the salt- and tobacco-monopolies which exist in Japan, the camphor monopoly seems to be a financial failure, in spite of the fact that the consumption of camphor is increasing steadily.

The revenues derived in the course of the last eleven years from the camphor-, salt-, and tobacco-monopolies are shown in the following table[2]): —

	REVENUE FROM THE		
	Camphor monopoly	Tobacco monopoly	Salt monopoly
1903/04 . . .	273 513 Yen	14 898 291 Yen	—
1904/05 . . .	712 609 „	27 462 007 „	—
1905/06 . . .	743 579 „	33 602 058 „	11 998 012 Yen
1906/07 . . .	1 163 826 „	32 574 484 „	23 232 385 „
1907/08 . . .	898 165 „	35 607 902 „	24 652 674 „
1908/09 . . .	221 714 „	49 304 568 „	15 606 242 „
1909/10 . . .	47 691 „	47 267 571 „	11 134 120 „
1910/11 . . .	93 317 „	50 936 126 „	11 060 131 „
1911/12 . . .	179 903 „	51 315 884 „	11 842 141 „
1912/13[3]) . . .	161 051 „	51 300 043 „	10 671 318 „
1913/14[3]) . . .	114 914 „	53 728 468 „	10 007 165 „

The Year Book in question also gives particulars (p. 28) of the cost to the State of the camphor monopoly. This amounted for the year 1904/05 to 59624 Yen; 1905/06 571827 Yen; 1906/07 762726 Yen and 1907/08 859747 Yen. The official statistics do not supply particulars of the outlay for subsequent years.

Possibly the cause of the unfavourable state of the Japanese camphor industry may be found in the competition of the synthetic product[4]). In order to maintain the competition with artificial camphor, the Monopoly has been compelled to regulate its quotations in harmony with those of the synthetic product. It is said that lately a German artificial camphor has been brought on the market of which the cost of production is 80/– p.cwt. Hence the Camphor Monopoly Bureau has reduced its price for B.B. camphor to 142/– p.cwt., but without success, and it is therefore not impossible that the quotation for this grade will have to be lowered to 100/–.

We have already on a previous occasion pointed out[5]) that the camphor monopoly hopes to find a fresh source of production of camphor in the distillation of camphor leaves. Experiments on a large scale in this direction are being conducted at present at the experimental station on the Tempai mountain (Fukuoka), which is situated in a camphor plantation[6]). This plantation contains about 58000 trees, which were planted in the year 1908. The daily capacity of the experimental station is 2000 gallons of oil, or 317 gallons from 400 lbs. of leaves (?). Four distillations are carried out daily, the camphor-content of the oil being estimated every three hours. The exhausted material is used as fuel.

At the present time there are over 500000 camphor trees on the Island of Kiu Shiu (Saikaido), distributed over an area of more than 60000 acres. As camphor

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[1]) *Chemist and Druggist* **84** (1914), 87. — [2]) *Finanz. u. wirtsch. Jahrbuch f. Japan* **13** (1913), 14. — [3]) Estimated. — [4]) *Handelsberichten* (The Hague) **7** (1913), 793. — [5]) Comp. *Report* April **1913**, 37; also page 36 of this *Report*. — [6]) *Daily Cons. and Trade Rep.*, Washington **16** (1913), 575.

leaves are easily transportable, it would be possible to work up the leaves from a large district in one central station. When distilling camphor wood it is inconvenient to go far afield from the collecting centre, because the wood, being heavy, is not so readily transportable.

Perhaps the projected scheme for a World's Camphor Trust, of which reports appear in the press from time to time[1]), may be connected with the alleged unfavourable position of the Japanese camphor industry. It is said that a preliminary understanding has already been reached between the Kobe houses and the European merchants, but that the negotiations with the United States have not yet led to the desired result.

There is very little further information concerning the camphor trade in China. In completion of the figures given on p. 33 of our last *Report* we may state that the shipments from the whole of China in the year 1912 reached 2484 piculs, of the value of 175975 Haikwan Taels[2]).

Judging from a Consular Report[3]) it is not impossible that there may be an increase in the camphor production of China. If rational methods of preparation were adopted, and if the trees were properly exploited, the camphor-output might be considerably enlarged. It is believed that four times as much camphor is now produced in China as is exported.

With regard to the production of camphor in Amani[4]), the hope of repeating on a larger scale the experimental distillation on the plantation, covering 15 hectares (= 37 1/2 acres), which has been laid down by the Administration of Forests at Wilhelmstal, could not be realized, owing to the lack of means of acquiring a suitable modern distilling-plant and of defraying the cost of distilling.

L. Beille and P. Lemaire[5]) report on the distillation of camphor from dry leaves and twigs[6]) which they had received from the Director of the Botanical Gardens at Konakry (French Guinea). In the year 1905 cuttings of camphor trees had been sent to Konakry, and by 1913 these had grown so much that the distilling-material referred to above could be gathered from them; 1000 grams of dry leaves yielded 16,5 grams (= 1,65 p.c.) of camphor. The young twigs yielded 0,375 p.c. of a camphor containing a great deal of oil, whereas the older twigs contained oil only.

In conclusion, reference remains to be made to an article which has appeared in a Dutch official publication[7]), according to which 108700 acres of virgin forest in Pahang (Malacca) have been set aside for camphor-production. The camphor-trees here occur only in the high-lying parts of the forest. It is estimated that only 1 p.c. of the trees contain camphor crystals. The natives of the virgin forest, the Sakais, have ceased to prepare camphor for such a long time that they have forgotten the very terms used by their ancestors in connection with the work in the days when camphor was still being collected. Only the headman of the tribe, the Pengkulu Kapur, is said to be able to judge whether a tree contains camphor or not. It is

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[1]) *Handelsberichten* (The Hague) **7** (1913), 894. — [2]) *Nachr. f. Hand., Ind. u. Landw.* **1913**, No. 145, p. 6. — [3]) *Daily Cons. and Trade Rep.*, Washington **16** (1913), No. 229, Oct. 1. — [4]) *Der Pflanzer* **10** (1914), 32; Comp. *Report* April **1912**, 34. — [5]) *Bull. de Pharm. de Bordeaux* **1913**, 521; *Annal. de Pharm.* **19** (1913), 534. — [6]) A symposium of distillations of camphor-leaves carried out in various countries is given in Gildemeister and Hoffmann's *Die ätherischen Öle*, 2nd Ed. Vol. II. p. 472. — [7]) *Handelsberichten* (The Hague) **7** (1913), 771.

said that he is able to smell this when an incision has been made into the tree, and no tree is allowed to be cut down until he has made sure that it contains camphor crystals. The preparation of camphor is very complicated, and a simplification of the process would be very welcome.

It would appear to us that the writer of the above article has confused Borneo-camphor with Laurel-camphor.

Canada Balsam Oil. A sample of Canada balsam received by us from Quebec ($\alpha_D + 5° 25'$; $n_{D22°}$ 1,52412), when distilled with steam, yielded a colourless oil, with an aroma resembling that of oil from the cones of *Abies pectinata*. Its constants were as follow: $d_{15°}$ 0,8614, $\alpha_D - 30° 36'$, $n_{D20°}$ 1,47809, acid v. 0, ester v. 3,7, soluble in 3 vols. a. m. of 90 p. c. alcohol. We only record the values here because Canada balsam oil is one of the less-known oils.

Cananga Oil. Business in this article has lately been very quiet indeed, although it has been possible to restore the prices to a reasonable level. The arrivals are not too heavy and the sales have moved within commensurate limits. We are, as always, in a position to supply our customers with the best quality at the lowest market prices.

Cananga oil is produced in two localities: it comes either from Serang or from Cheribon. Most of it comes from the first-named place; the Cheribon oil is not so well-known. Its quality is equally good as that of the oil from Serang, but its odour is somewhat sharper or, to express it more accurately, somewhat more penetrating, a property which is preferred by some buyers, while others do not appreciate it so much. We only mention this because oils of this kind have lately repeatedly been seen in the market. We have not, however, met with any adulterated oil.

At Buitenzorg[1]) cananga oil has been found to possess the following characters: $d_{15°}$ 0,9061 to 0,916, sap. v. 10,3 to 25,2, sap. v. after acet. 47,7 to 67. All the samples were soluble in one-half their vol. of 95 p.c. alcohol.

Cape Oil. "Cape" leaves, from which Roure-Bertrand Fils[2]) some time ago prepared an essential oil with a pleasant odour, have been subjected to a thorough botanical examination by E. G. and A. Camus[3]). The leaves were found to be derived from an as yet unknown species of *Popowia* (N. O. *Anonaceæ*), to which the authors have given the name of *P. Capea*. *Popowia Capea*, E. G. et A. Camus is a small, creeping shrub which occurs exclusively in the dense forests of the eastern part of the Ivory Coast, in the Attié and Agnis regions. Even there it is somewhat rare. It is a remarkable fact that, as a rule, the fruits contain no seeds, because almost invariably they are transformed into galls by the stings of insects. Only a restricted use is made of *Popowia Capea* on the Ivory Coast. A parcel of dry leaf and stalk weighing about 200 grams costs locally 20 cents, and in the markets outside the growing-district the price is much higher still. For purposes of use, the raw material, consisting of the stalks and leaves, is first coarsely broken up and then macerated with cold water. The extract thus obtained is then used in the bath without further preparation.

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[1]) *Jaarb. dep. Landb. in Ned.-Indië*, Batavia, **1912**, 195. — [2]) *Berichte von Roure-Bertrand Fils* October **1911**, 43; *Report* April **1912**, 37. — [3]) *Berichte von Roure-Bertrand Fils* October **1913**, 3.

We are unable in this place to enter into a detailed and precise morphological and anatomical description of *Popowia Capea*. We only note that the essential oil is localised in special cells, which are usually isolated, but that it occurs in all the divisions of parenchyma of the stalks and the leaves.

From 42 kilos leaves the authors obtained 246 grams (= 0,59 p.c.) of a volatile oil. By far the greater part (160 grams) was heavier, the remainder (86 grams) lighter, than water. The analytical constants of the entire oil and of the heavy and light fractions respectively are as follow: —

	Entire oil	Heavy fract.	Light fract.
d_{200}	1,0042	1,0081	0,9960
α_D	+ 76° 56′	+ 90° 54′	+ 51° 26′
Acid v.	2,8	1,5	3,7
Sap. v.	166,1	192,3	123,2
Sap. v. after acet.	239,9	248,3	218,4
Solubility in 80 p.c. alc.	1 vol., afterwards turbidity.	1 vol., afterwards very pronounced turbidity.	1 vol., afterwards marked turbidity.
Solubility in 95 p.c. alc.	0,5 vol. afterwards slight opalescence.	from 3 vols clearly marked opalescence.	0,5 vol. afterwards very slight turbidity.

Acetylation causes a very great diminution in the rotation; in the entire oil to + 13° 48′, in the heavy fractions to + 18° 4′ and in the light fractions to + 5° 12′.

6 p.c. of the oil combines with bisulphite.

The saponification liquors yielded a very thick, oily liquid, with a clearly perceptible odour of cinnamic alcohol. The liquid did not crystallise.

Caraway Oil. The report of a shortage in the Dutch caraway crop which we published last October has been confirmed in every respect. The oil-content of the caraway of the 1913 crop was surprisingly small, and the Dutch caraway oil manufacturers have apparently derived little satisfaction from their operations in that season. The advances in price which were prognosticated have only been realized in a very modest degree, because large stocks of caraway from the record-crop of 1911 continued to depress the market. The prospects for 1914 are said to be unfavourable. It is true that so far no official data are available from the Department of Agriculture, but from certain districts come reports that the area under cultivation is below that of 1913, and that a number of fields have been ploughed up because the plants had stood the winter badly. As a result the prices of caraway of the new seed (Aug.-Sept. delivery) have for the present advanced considerably. The first Government reports on the condition of the plantations are usually published on 15th April, and nothing definite can therefore be said at present as to the future course of the market. We may, however, place on record the fact that the area under cultivation in the year 1913 amounted to 5310 hectares (2991 hect. in 1912), which yielded 58976 bags of caraway, and not as the first estimate had it, 25000 bags.

Our trade in all varieties of caraway oil has been normal and we were unable to notice any decrease in the interest shown by the liqueur-manufacturers in caraway-liqueurs, although generally speaking it is impossible to ignore the tendency to turn away from the old-established, simple liqueurs, in which competition is now so heavy, and to take up the manufacture of specialities. As is well-known, we purify our caraway oils by a special process and in respect of flavour we are therefore able to supply the very best that can be had in the article.

Cardamom Oil. The conditions of prices in the cardamom market have not yet improved, and so far as our information goes, no improvement is to be expected within a foreseeable time. We have therefore been obliged to maintain our present quotations for cardamom oil. A parcel of so-called wild cardamoms has recently been offered from London and, we hear, has been purchased by a firm in our branch of industry. To our certain knowledge, oil prepared from such cardamoms, although cheap, is in other respects wholly worthless, and its employment in the manufacture of comestibles may cost the users dear.

Cascarilla Oil. Our stocks are again contracting alarmingly, and in view of the scarcity of raw material for distilling it may be extremely difficult to replenish them in good time. There is no doubt that the price will continue to be as high as it is now.

Cassia Oil. The pronounced flatness of the market to which we referred in our last *Report* has continued during the winter, and prices have fallen to a level such as has not been known for many years. It cannot even approximately be stated wherein lies the cause of this fact. All Chinese cassia-products, however, have depreciated to such an extent that they bring losses to all concerned in the trade, and the only feasible assumption is that the conditions of insecurity prevailing in the country have induced the Chinese to turn their products into cash as soon as possible, and that the slump has been caused by the want of proportion between supply and demand. The present prices should be a stimulant to the laying-in of plentiful supplies, for the probability of a further decline in the market is slight, seeing how low is the present value.

It is scarcely necessary for us to point out specially that we are continuing our efforts to discover cassia oils free from colophony, but we have to report to our regret that in this endeavour we continue to meet with great difficulties[1]). The suppliers are only willing to guarantee a definite aldehyde-content; they still remain unwilling to guarantee that the oil will stand the lead-acetate test, as it is said to be impossible to induce the distillers always to supply an oil which is free from colophony.

We are not abandoning the hope of ultimately achieving a measure of success in this matter. If the exporters will make up their minds to present a solid front to the producers, and the latter find that they can only sell pure oil, it should be possible to bring about a better state of things.

According to a report by the Consul General of the United States in Hong Kong[2]) the prices of cassia oil have fluctuated greatly owing to speculative enterprises. The quotation for the best grade of cassia oil per Picul of 133$^1/_3$ lbs. ranged from $ 200.— local currency (= $ 101.— gold) in January to $ 205.— local currency (= $ 104.— gold) in April and then slowly fell to $ 176.— in November, while at the close of the year it reached $ 178.— (= $ 86.25 gold). The value of the cassia oil exports to the United States in the year 1912 reached $ 76 682, as compared with $ 67 696 in the year 1913. The shipments to Europe exceeded those of the previous year by 50 p.c.

Cedar Wood Oil. We are so favourably placed with regard to this article (which is of very great importance in soap-making), that we are able to offer specially favourable terms for large contracts. In comparing prices, however, the fact should

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[1]) *Report* April **1913**, 40; October **1913**, 38. — [2]) *Daily Cons. and Trade Rep.*, Washington **17** (1914), No. 56, p. 906.

be borne in mind that we only supply the best quality, and that there are therefore certain limits to our capacity of meeting the market.

Celery Oil. The prices have given way a little during the last few months under the pressure of cheap offers from France. Apparently more has been produced in that country than can be sold before the new crop comes in, so that the holders now find themselves compelled to market their oil as best they can, even at a loss. In these conditions we have abstained from taking up the manufacture ourselves, which we would otherwise have been able to do profitably at our Barrême distillery. Moreover the price of celery-seed was out of proportion to the cheap offers of celery oil by the French producers.

Cinnamon Oil, Ceylon, German Pharmacopœia V. The prices of the raw material have remained firm, and the demand increased to such an extent in the course of the winter, that our factory was at times unable to keep pace with it. The advances in price which have been declared were therefore unavoidable, the more so because the oil-yield of several parcels of bark which came to hand fell much below the usual average. The situation of the article is such that lower prices are not to be expected in the near future.

Cinnamon Leaf Oil. This oil has at times been very scarce, but we have quite lately received a small parcel of excellent quality from the Seychelles, and we are therefore able to satisfy the needs of, at any rate, our regular customers.

Citronella Oil. During the winter the "cif" quotations of Ceylon citronella oil have been more or less maintained at their previous level of 1/6 s. d., and no material change is in prospect so far as can be foreseen, unless (which is hardly to be expected), the demands on the part of consumers should attain unexpected dimensions, and should lead to an increase in the prices. On the other hand, if the demand should become weaker, it is to be expected that citronella oil will follow the general downward tendency which has signalized the position of the principal commercial essential oils for some time past.

The exports from Ceylon up to 2nd March 1914 were

258 135 lbs.,

compared with 126 531 „ in the corresponding period of last year; that is to say they have more than doubled.

England and the United States being plentifully supplied, it is not expected that these two chief consumers will show much interest in the article for some time to come.

The citronella shipments in the years 1913 and 1912 were as follows:—

	1913 lbs.	1912 lbs.
England	643 485	632 652
France	59 463	35 068
Germany	296 121	167 389
Western Australia	1 134	2 464
South Australia	4 592	6 183
Victoria	18 075	32 101
New South Wales	29 950	21 232
Queensland	4 958	2 893
Carry forward	1 057 778	899 982

	1913 lbs.	1912 lbs.
Carried forward	1 057 778	899 982
New Zealand	1 147	1 582
U. S. of America	504 705	493 333
India	10 047	4 555
Straits Settlements	432	—
China	15 134	7 941
Philippines	—	—
Japan	13 238	12 913
Total	1 602 481	1 420 306.

Since our last *Report* there has been a not inconsiderable change in the market position of Java citronella oil. The driving-up of prices to which we referred in October 1913 has had for its result the establishment of a whole series of new distilleries and plantations in Java, the owners of which desired to profit from the exceptionally high prices which were paid for Java citronella oil at the end of last year. It is said that some of those engaged in the industry in Java have allowed themselves to be deluded by brokers, who had held out to them the prospect of large gains, into selling enormous quantities for delivery in the present year and in 1915. As always happens in such cases, buyers were of course found at good prices and the latter, with their contracts in their pockets, now believe themselves to be sufficiently covered for the whole of the year. In our opinion, however, they will find themselves bitterly disappointed, for we do not believe that even one-half of the quantities sold will be delivered. The planting of Sereh-grass is comparatively costly and as, moreover, it is necessary to lay down a plant of some sort or other for distilling the grass, some of the new "manufacturers" (so we are informed from Java) have already lost their enthusiasm for the business. And when the many new undertakings in the island begin to understand that is not possible always to realize such prices as they may have thought, other producers, or such as contemplate going in for the industry, will simply let their contracts slide, and will allow the buyers in Europe to do as they please.

Few sales have been made lately. On the one hand, the fact that the price of geranium oil has fallen very considerably has exercised a certain indirect influence upon the citronella oil market, and on the other, nobody now cares to buy unless he is absolutely in need of oil. Most firms still calculate upon receiving a considerable part of the oil which they have bought for delivery during the current year. We believe, however, that we shall not be wrong in assuming that last year's experience will repeat itself this year; the small new works in Java will deliver nothing or next to nothing, and towards the middle or the end of the year a strong demand will again set in for the article. It is obvious that the prices will then become firmer again. Hence, in our opinion, the position of the market will develop on similar lines as last year.

There have lately been considerable differences in the quality of the oil. Judged by analytical results there have only been few cases of adulteration, but some of these have been of a very gross character. For the rest, the oils that have come on the market may be described as pure and unadulterated, although, as already stated, the Java oils have lately shown differences, often somewhat considerable, especially in respect of their citronellol- and geraniol-content.

We are now able, as the result of a further series of observations made by us, to amplify the statements of the geraniol- and citronellal-contents respectively of citronella oil, which we made in our *Report* of April **1913**, p. 44. The estimation of geraniol was carried out by the method previously described (*Report* October **1912**, p. 43). We have lately carried on the estimation of citronellal exclusively by the oximation-method (*ibidem* 42), as this method has been shown to give the most equable results. The limits of value ascertained by us were as follow:—

	Java Citronella Oil	Ceylon Citronella Oil
Geraniol . . .	26 to 44,4 p. c.	26,7 to 38,8 p. c.
Citronellal . .	23,4 to 50,1 p. c.	5,5 to 10,5 p. c.

Among the Java citronella oils those with a high citronellal content were generally distinguished by a particularly delicate aroma; these samples, moreover, had a very low sp. gr.

In view of the great scarcity of Java citronella oil, of which the supply is insufficient to meet the European and American demand, Prof. W. Dunstan has suggested to the Ceylon Chamber of Commerce whether it would not be worth while to cultivate in Ceylon on a large scale[1]) the Maha Pengiri or Winter's Grass variety of the plant, from which the Java oil is obtained. So far, this variety of grass is very little grown in Ceylon. If the cultivation is to be made to pay the oil would have to realise better prices than it now commands, for although Maha Pengiri grass requires a better soil and greater care than does Lenabatu grass, both oils realise the same price in Ceylon, whereas Java citronella oil is commercially worth more than twice as much as Ceylon citronella oil. According to Drieberg, of Peradeniya, the cultivation of citronella grass in Ceylon is not increasing, and although a little more grass is now grown in the district of Tangalle than formerly, the cultivation in the district of Galle-Matara has been superseded by that of rubber. This statement, however, is not in accord with that in the *Ceylon Handbook*, according to which there were in September 1913 5293 acres under citronella grass, as compared with 4359 acres in 1911. The demand for citronella oil appears to be continually increasing, and in spite of the larger oil-shipments from Ceylon the prices have not declined to any appreciable extent, neither have there been any considerable accumulations of stock in Europe or America. Up to December 8, 1913 the shipments from Ceylon amounted to 1 430 137 lbs., or 159 288 lbs. more than in the corresponding period of the previous year. Of this quantity 565 162 lbs. were shipped to England (567 670 lbs. in 1912), 451 531 lbs. to the United States (436 413 lbs. in 1912) and 264 661 lbs. to Germany (153 087 lbs. in 1912).

Many years ago we[2]) detected the presence in Ceylon-citronella oil of a sesquiterpene with the low specific gravity 0,8643 (15°). It is probable that this body may be identical with an aliphatic sesquiterpene $C_{15}H_{24}$ which has been discovered in Java citronella oil by F. W. Semmler and K. E. Spornitz[3]), and which they call sesquicitronellene. At the time we separated the sesquiterpene from methyleugenol by repeated washing with 60 and 70 p.c. alcohol. Semmler and Spornitz have applied the same method to a sesquiterpene fraction of the Java-citronella oil, which we had placed at their disposal. By means of repeated fractionation they succeeded in isolating the sesquicitronellene in the pure state from the product which had been distilled over sodium. The body possessed the following characters: b. p. 138 to 140° (9 mm.), $d_{20°}$ 0,8489, $\alpha_D + 0° 36'$, n_D 1,53252. Curiously enough the molecular refraction was found to be 74,53, whereas the calculation for $C_{15}H_{24}/\overline{4} = 69{,}6$. A similar high degree of exaltation has been observed in the aliphatic terpene, ocimene. The reduction of sesquicitronellene with sodium and alcohol gave rise to dihydrosesquicitronellene, $C_{15}H_{26}$. The fact that it is possible to reduce the sesquiterpene with sodium and alcohol is evidence that, like myrcene and ocimene, it contains two conjugated double bonds. Dihydrosesquicitronellene boils between 131 and 133° (12 mm.): $d_{20°}$ 0,8316, $\alpha_D \pm 0°$, n_D 1,4800. With platinum and hydrogen the sesquiterpene afforded octohydrosesquicitronellene, $C_{15}H_{32}$: b. p. 115 to 117° (9 mm.), $d_{20°}$ 0,7789, $\alpha_D \pm 0°$, n_D 1,43518. By the aid of concentrated

[1]) *The Chemist and Druggist* **84** (1914), 3. — [2]) *Report* October **1899**, 23. — [3]) *Berl. Berichte* **46** (1913), 4025.

formic acid sesquicitronellene may be inverted into a cyclic sesquiterpene (*cyclo*sesquicitronellene). The inverted sesquiterpene can be no further reduced with sodium and alcohol, which fact leads the authors to assume that the ring-formation has been effected by the aid of one of the double-bonds, the conjugation being suspended. Upon ozonising the sesquiterpene-fraction, after washing it out with alcohol, a paraffin $C_{20}H_{38}$ was isolated from the ozonide decomposition-products. It is still doubtful whether this paraffin is a natural constituent of citronella oil, or whether it had got into the oil by sophistication, say with petroleum[1]).

By reacting with sodium upon the sesquiterpene fraction which had been washed out with alcohol and distilling off the hydrocarbons, a tertiary, doubly-unsaturated sesquiterpene alcohol, $C_{15}H_{26}O$, was obtained.

In the course of preparing geraniol from Ceylon citronella oil, F. Elze[2]) has obtained a small yield of a fraction boiling between 150 and 165° (5 mm.) from which, after saponification and steam-distillation (a considerable proportion being lost in the manipulation), he obtained an oil which, after being treated with phthalic anhydride and the phthalate being worked up in the usual manner, afforded farnesol. The alcohol possessed the following constants: b. p. 145 to 146° (5 mm.), $d_{15°}$ 0,895, α_D inactive. It occurs in the oil both in the free and in the esterified state, the proportion being from 0,2 to 0,3 p. c.

Clove Oil. However much the reports received may differ according to the mood of their authors, the fact remains that the 1913/14 crop may be described as a plentiful one, the average estimate of the yield being 185 000 bales. The market has accordingly continued to show a falling tendency, which was confirmed by the very reserved attitude of consumers. A few weeks ago, however, the movement of retrogression came to a standstill. Numerous speculators who were "discounting the fall" had sold considerable quantities in London and other centres of the trade for future shipment, and as these operators are now forced to cover themselves the sellers have withdrawn from the market or have advanced their quotations accordingly, while they are everywhere trying to engineer a bullish feeling. The tendency is made firmer still by the report that the result of the summer crop of 1914 will only be very moderate. The estimates vary from 50 000 to 100 000 bales.

According to the statements of our informants the exports from Zanzibar and Pemba between 1st August 1913 and 1st March 1914 amounted to about 165 000 bales, of which were shipped

to Europe	about	49 000	bales
„ America	„	19 000	„
„ Bombay	„	60 000	„
to other Ports	„	7 000	„
Total	about	135 000	bales, while 30 000 bales have

been put in warehouse in Zanzibar, it is said for account of some important speculators at Bombay.

The stocks in Europe and America, which as a rule increase considerably at this time of the year, especially after a satisfactory crop, are now on the other hand contracting, and may even be called very small. Moreover, it is said that almost the

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[1]) Comp. *Report* April **1913**, 46. — [2]) *Chem. Ztg.* **37** (1913), 1422.

whole of them is already under definite control. The stocks in London, Holland, Hamburg, and New York on 28th February were as follows: —

1914 . . .	25000 bales	1907 . . .	39000 bales
1913 . . .	23000 „	1906 . . .	43000 „
1912 . . .	41000 „	1905 . . .	47000 „
1911 . . .	41000 „	1904 . . .	42500 „
1910 . . .	75000 „	1903 . . .	73000 „
1909 . . .	62000 „	1902 . . .	101000 „
1908 . . .	62000 „		

Taking all these factors into account, it is believed that the conclusion is warranted that for some time to come the market will unquestionably be faced with rising prices, especially because, as stated above, the consumers are only sparingly supplied, as a result of the reserve they have practised thus far. In view of the incalculability of the market we will not venture to criticize this view.

We regret that on the present occasion no statistical material of any description is available.

A recently published work by J. E. E. Caster[1]) on the Island of Pemba contains a description of the harvesting of cloves. During the clove-harvest men, women and children spend almost the whole day in the tops of the trees. The picked bunches of cloves are dropped into a cloth which is tied round their necks. Afterwards the cloves are separated from the stems and spread out on grass mats in front of the houses to dry in the sun. The cloves must be picked before the buds have burst, otherwise the fruit is of small value. They are picked as soon as they turn pink. If the picking is delayed too long, the bud at the end bursts, and a starry white little flower appears. After a day or two the flower fades and falls, the clove swells rapidly and darkens till it looks like a purple olive. It has a large stone inside and the flesh is also purple and tastes of oil of cloves. The fruit is eaten by monkeys, but by no other animal.

It is difficult to grow clove trees from seed, as the young plants are very delicate, require a shady, sheltered position, and grow very slowly.

The Arabs do not prune the clove trees, with the result that a thick tangle of branches grows up, and after this the trees only bear on the upper branches, which makes harvesting very difficult and in part impossible.

It has been proved that by rational pruning the yield can be increased by 30 p.c. Nor are the clove trees in Pemba manured, though it would probably pay to do so. The normal yield is about 35 lbs. of dried cloves per tree.

Two samples of clove oil distilled in the island of Mauritius have been submitted to us by the Imperial Institute in London for our opinion. Their characters were as follows: $d_{15°}$ 1,0614 and 1,0681, α_D — 0° 24′ and — 0° 20′, $n_{D20°}$ 1,53361 and 1,53723, eugenol-content (estimated with 3 p.c. soda liquor 93 p.c. and 96 p.c.; soluble in 1,5 and in 1,2 vols. a. m. of 70 p.c. alcohol. We only refer to the samples here because their origin is of interest.

Clove Leaf Oil. A clove leaf oil from Zanzibar has been examined at the Imperial Institute in London[2]). Its characters were as follows: $d_{15°}$ 1,0652, sol. in 1,1 a.m. vols. 70 p. c. alcohol. The oil contained 85,7 p. c. eugenol.

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[1]) *Pemba, the Spice Island of Zanzibar; Chemist and Druggist* **83** (1913), 825. — [2]) *Bull. Imp. Inst.* **11** (1913), 438. Comp. *Report* November **1908**, 48.

Several years ago we published in our *Reports*[1]) a few brief particulars of Seychelles clove leaf oil, and we are now able to add to these a few data, as we have in the meantime had an opportunity of examining further oils from this source. The constants now observed range within the following limits: $d_{15°}$ 1,0324 to 1,0493, α_D — 1° 40′ to — 1° 53′, eugenol content (estimated with 3 p. c. soda liquor) 78 to 87 p. c., soluble in 1 to 1,5 vols. of 70 p. c. alcohol; when more alcohol is added turbidity occurs in a few cases. Three samples of clove-leaf oil distilled in Mauritius, which have been received by us from the Imperial Institute in London, exhibit exactly similar characters. We record the values below: —

$d_{15°}$	α_D	$n_{D20°}$	Eugenol content	
1,0626	— 1°	1,53814	93 %	Soluble in 1 vol. a. m. of 70 p. c. alcohol.
1,0610	— 0° 50′	1,53639	92 %	
1,0671	— 0° 50′	1,53914	92 %	

Copaiba Balsam Oil. It is a familiar fact that several investigations[2]) have established the presence in African copaiba balsam oil of considerable proportions of a dextrorotatory sesquiterpene, possessing the properties of cadinene, but affording a lævorotatory hydrochloride. In addition to this sesquiterpene, Deussen[3]) has found that the oil contains about 0,9 p. c. of β-caryophyllene. Having occasion to prepare cadinene from an African copaiba balsam oil, we examined the first runnings of the sample, and submitted 600 grams thereof to careful fractionation. We obtained the following principal fractions with more or less constant b. p.: —

1. 119 to 120° (10 mm.); 246 to 248° (ord. press.) 10 %; α_D — 13° 7′.
   248 „ 250° („ „) 70 %
   250 „ 251° („ „) 10 %
2. 123 to 125° (10 mm.); 258 to 263° (ord. press.) — ; α_D — 6° 52′.
3. 130 to 133° (10 mm.); 267 to 270° (ord. press.) 20 %; α_D + 50°.
   270 „ 273° („ „) 70 %

The principal fraction (No. 3) had the same b. p. as cadinene. The other characters of the "cadinene-fraction" isolated from the oil were: $d_{15°}$ 0,9261, $[\alpha]_D$ + 60° 40′, $n_{D20°}$ 1,51112.

Fraction 2 (20 gr., α_D — 6° 52′) was tested for caryophyllene. With glacial acetic and sulphuric acids it afforded no caryophyllene alcohol, but when nitric oxide was passed into the ethereal solution according to Deussen's method[2]), we obtained 2,33 p. c. of a nitrogenous body, derived from β-caryophyllene. (m. p. 155 to 156° from acetone). Deussen obtained 25 p. c. of this substance from a fraction (α_D — 4° 36′). The oil examined by us, therefore, must have contained much less β-caryophyllene than did Deussen's.

Fraction 1 (100 gr.; $d_{15°}$ 0,9077; $[\alpha]_D$ — 13° 21′; $n_{D20°}$ 1,48943); only afforded the smallest traces of the nitrogenous body from β-caryophyllene, and can therefore have contained next to nothing of this sesquiterpene. It yielded neither a solid nitrosochloride nor a nitrosite, but it afforded 30 p. c. of a solid hydrochloride, m. p. 117 to 118° and $[\alpha]_D$ — 36,38° in a 5,09 p. c. chloroform solution. These characters, as well as fusion with *l*-cadinene hydrochloride (in which manipulation the m. p. was also found to be

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[1]) *Report* October **1907**, 37; November **1908**, 48. — [2]) Comp. *Report* October **1909**, 31. — [3]) *Liebigs Annalen* **388** (1912), 139; *Report* October **1912**, 149.

117 to 118°), showed it to be identical with the last-named body. When treated with sodium acetate in a glacial acetic acid solution the hydrochloride yielded a cadinene possessing the following properties: b. p. 273 to 275°, $d_{15°}$ 0,9229, $[\alpha]_D$ — 116,73°, $n_{D20°}$ 1,50651; when treated with hydrochloric acid gas cadinene hydrochloride, m. p. 118, was again formed.

The liquid chlorides freed by suction from the cadinene hydrochloride of fraction 1 were examined for the presence of other chlorides. As they could not be distilled *in vacuo* they were boiled with their own weight of sodium acetate in glacial acetic acid solution, for the purpose of eliminating the hydrochloric acid, and the resulting oil was fractionated *in vacuo*. Of three equal fractions thus obtained: —

a) 111 to 121° (7 mm.), b) 121 to 130°, c) 130 to 135°.

b) and c) afforded copious proportions of cadinene hydrochloride m. p. 117, 5 and 118°, only fraction a) failed to yield a solid product. The liquid chlorides of fraction 1 therefore behaved for the major part exactly like the solid chloride, and must therefore have consisted likewise in the main of cadinene hydrochloride.

The investigation showed that the first runnings of African copaiba balsam oil contain a lævorotatory sesquiterpene, which, although differs materially from cadinene in regard to its physical properties: —

	b. p.	$d_{15°}$	$[\alpha]_D$	$n_{D20°}$
Sesquiterpene .	246 to 251°	0,9077	— 13° 21′	1,48943,
Cadinene[1]) . . .	271 „ 273°	0,9215	—105° 30′	1,50647,

yet affords cadinene hydrochloride. It is probably closely related to cadinene.

So far, three sesquiterpenes are known which, when treated with hydrochloric acid gas, afford lævorotatory cadinene hydrochloride; namely: —

1. *l*-cadinene proper.
2. The *d*-sesquiterpene of West Indian sandalwood oil and of African copaiba balsam oil.
3. The *l*-sesquiterpene, b. p. 246 to 251°, of African copaiba balsam oil.

For the following reasons this result is of general interest: In by far the great majority of instances the identification of cadinene in essential oils has not been achieved by isolating the body as such, but by preparing its hydrochloride from fractions of which the b. p. usually lay between 250 and 270°, or frequently "from the sesquiterpene fraction". It is therefore not impossible that in many cases cadinene has been assumed to be a constituent of essential oils which possibly contained another sesquiterpene which also afforded cadinene hydrochloride. Hence, the isolation of cadinene hydrochloride by itself can no longer be regarded as proof of the presence of cadinene.

Coriander Oil. Business has been very slow and the experience of the past year confirms the fact that the consumption of this article, formerly so important, has fallen off greatly. Large quantities still remain unsold, not only in the second hand, but also in Russia, and the market must be described as flat. Of course, if the crop this year were a failure the situation would be changed at one stroke. Our recently-introduced terpeneless coriander oil has found favour everywhere, its exceptional solubility constituting an advantage which makes it indispensable to most liqueur-manufacturers who have tried it.

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[1]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd Ed. Vol. I, p. 329.

Although the cultivation of coriander in Russia has been declining for years, the crop of 1913 nevertheless was about 350 000 kilos, the average yield of the area under cultivation having been very satisfactory.

Moravia, Hungary and Thuringia have not produced any quantity of coriander worth mentioning; at any rate the product of those countries has long ceased to be of any importance for distilling purposes.

Cubeb Oil. Plentiful offers of excellent raw material, rich in oil, have further depressed prices, and it has therefore been possible, in the course of the winter, to reduce the quotations repeatedly, the more so because the demand for oil of cubebs has kept within very moderate limits.

Oil of Cymbopogon coloratus. Oil from *Cymbopogon coloratus*, Stapf[1]) is one of those oils which had been very little investigated, until, quite recently, E. Goulding and J. C. Earl[2]) examined it thoroughly. The sample examined by them was distilled from green herb in the Fiji Islands. Yield about 0,35 p.c. $d_{15°}^{15°}$ 0,912, $[\alpha]_{D\,24°}$ — 10,31°. The oil was found to contain 23 p.c. of geraniol (estimated by the phthalic anhydride method), and about 10 p.c. of geranyl acetate. For purposes of identification the geraniol was converted into the diphenylurethane, m. p. 82°. Other constituents identified were: 7,5 p.c. terpenes (possibly a mixture of *l*-limonene with one or several other terpenes), 40 p.c. aldehydes, principally citral, 0,75 p.c. acetic acid and 0,75 p.c. phenols. Among the phenol-like constituents was an inodorous body, m. p. 142°.

Cypress Oil. Whenever an epidemic of whooping-cough breaks out, the medical faculty is glad to remember this well-established specialty, the action of which is positively astounding, especially in cases where the disease is still in its first stage. In making this statement it is of course presupposed that the pure distillate from branches of *Cupressus sempervirens* is employed, such as we prepare in our factory at Barrême, and not an oil made from those degenerate varieties which have none, or only a slight, medicinal efficiency. We shall be pleased to supply pharmacists with literature for distribution among the medical profession.

Oil of Dacryodes hexandra. Many years ago we referred to a paper by A. More[3]) on oil from the resin of *Dacryodes hexandra*, Griseb. (N. O. *Burseraceæ*). According to More the resin, when distilled by steam, affords about 16 p.c. of a readily volatile oil, which distils over between 156 and 180°, leaving from 12 to 13 p.c. of residue. In the fraction boiling between 156 and 163°, More found *l-a*-pinene (monohydrochloride, m. p. 128°), while the fraction boiling between 173 and 176°, when saturated with dry hydrochloric acid gas, afforded a hydrochloride, m. p. 71°, crystallising at — 10°, which fact pointed to the presence of sylvestrene. As the fraction from which the hydrochloride was prepared was strongly lævorotatory, the occurrence of *l*-sylvestrene in an essential oil was rendered highly probable for the first time by this investigation. But as More's research was only carried on with very small quantities of material, which did not permit of an exhaustive identification of the terpene said to be sylvestrene, it remained desirable to confirm his results.

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[1]) Comp. *Report* April **1911**, 58; October **1912**, 52. — Gildemeister u. Hoffmann, *Die ätherischen Öle*, 2nd Ed., Vol. II, p. 256. — [2]) *Proceed. chem. Soc.* **30** (1914), 10. — [3]) *Journ. chem. Soc.* **75** (1899), 718; *Report* October **1899**, 28.

A good many years ago we distilled a small parcel of dacryodes resin[1]), from which we obtained about 16 p.c. of a yellowish, mobile oil with an agreeable aromatic odour, this result confirming More's statements. The specific gravity of our oil was 0,8875 at 15°, its rotation was α_D — 13° 20′.

We have now submitted this oil to closer investigation, and have found it to possess the following characters: $d_{15°}$ 0,8880, α_D — 13° 40′, acid v. 1,2, ester v. 11,2, ester v. after acet. 56,0. With the object of isolating and identifying the sylvestrene we first fractionated 100 gr. of the sample: —

1.	B. p. 156 to 170°	10 %	α_D — 21°
2.	„ 170 „ 173°	30 %	α_D — 19° 50′
3.	„ 173 „ 178°	20 %	α_D — 17° 30′
4.	„ 178 „ 182°	15 %	α_D — 14° 45′
	Residue		dextrorotatory.

In order to obtain the hydrochloride we passed dry hydrochloric acid gas up to saturation point into the cooled ethereal solution of all the fractions, and drove off the ether after leaving standing for 3 days. The hydrochloride separated out under strong cooling, and was pressed on cooled porous tiles.

Fraction 2 (sp. gr. 0,8689 at 15°), when treated in this manner, afforded in addition to portions which had remained liquid, *l*-sylvestrene hydrochloride. When recrystallised from alcohol it had m. p. 68° and sp. rot. $[\alpha]_D$ — 21,3° (in a 4,3 p.c. ethereal solution).

Fraction 3 ($d_{15°}$ 0,8708) yielded a substance melting at 63°, sp. rot. $[\alpha]_D$ — 19,5° (in a 6,6 p.c. ethereal solution). This product was apparently rather less pure than the foregoing.

Fraction 4 afforded a product much contaminated by liquid hydrochloride, of which the m. p., in spite of repeated recrystallisation, did not surpass 50°.

We were able to prove the presence in fraction 1 of α-pinene (b. p. 156 to 160°) from its nitrolbenzylamine compound (m. p. 122°), whereas portions boiling between 164 and 167° were repeatedly tested for β-pinene without result. The fraction boiling between 164 and 167° appears to contain traces of camphene, inasmuch as after hydration and saponification a small quantity of oil was obtained which, after treatment with potassium permanganate, had a well-defined odour of camphor.

When treating a somewhat larger portion of oil (1500 gr.), which we distilled first with steam, then *in vacuo* and finally over sodium, we obtained on the whole similar results as with simple fractionation. We observed, during this manipulation, that the *l*-sylvestrene which was present in the oil appears to be inclined to resinify and that its specific gravity is therefore only low when it is freshly-distilled.

Finally we obtained the following fractions: —

1.	154 to 162°	8 g.	α_D — 21° 40′	$d_{15°}$ 0,8633
2.	164 „ 167°	106 g.	α_D — 25° 10′	$d_{15°}$ 0,8637
3.	168 „ 171°	438 g.	α_D — 22° 0′	$d_{15°}$ 0,8640
4.	171 „ 172°	130 g.	α_D — 19° 47′	$d_{15°}$ 0,8650
5.	173 „ 175°	200 g.	α_D — 19° 2′	$d_{15°}$ 0,8652
6.	174 „ 178°	190 g.	α_D — 18° 12′	$d_{15°}$ 0,8663
7.	85 „ 90° (4 to 5 mm.)	170 g.	α_D + 12° 43′	$d_{15°}$ 0,9465

[1]) *Report* October 1901, 20.

The purest form of hydrochloride, m. p. 68, was again afforded by the fraction boiling between 168 and 171°, whereas the hydrochloride isolated from the three fractions boiling between 171 and 178° mostly melted as low as 63°, acquired a yellow colour when exposed to light, and gradually became somewhat decomposed. In addition we obtained considerable proportions of the chloride, which remains liquid in a freezing mixture.

For the further identification of the *l*-sylvestrene we warmed 20 gr. hydrochloride from fraction 173 to 175°, m. p. 68 and $[\alpha]_D$ — 19,5° with 20 gr. aniline and 5 cc. alcohol on wire-netting until aniline hydrochloride was separated out; after which we distilled it by steam, adding acetic acid. The *l*-sylvestrene regenerated by this method (about 10 gr.) possessed the following characters: b. p. 172 to 180°, $d_{15°}$ 0,8604, α_D — 45° 0′, $n_{D20°}$ 1,47838. With acetic anhydride and sulphuric acid, the *l*-sylvestrene gave the familiar intense blue coloration, and also a small last runnings, b. p. 180 to 185°. After three months the preparation had become much resinified.

As a check-test we diluted with aniline under similar conditions a preparation of *d*-sylvestrene hydrochloride, m. p. 71°. The principal portion of the regenerated *d*-sylvestrene boiled between 178 and 182°; its constants were as follows: $d_{15°}$ 0,8659, α_D + 54° 17′; $n_{D20°}$ 1,47936. This product also, when treated with acetic anhydride and sulphuric acid, gave the blue coloration and was partly resinified after three months' standing. A small last runnings boiling between 182 and 184° was less optically active: α_D + 41° 43′.

When the deep-brown coloured liquid chlorides were decomposed with aniline we obtained a rather impure sylvestrene (b. p. 170 to 185°; $d_{15°}$ 0,8712; α_D — 13° 40′) which nevertheless gave the blue coloration with sulphuric acid and acetic anhydride. It was a noteworthy circumstance that the fractions of the original oil did not give this colour-reaction, although they were certainly rich in sylvestrene.

The terpene which results from the decomposition of sylvestrene dihydrochloride, as Haworth, Perkin and Wallach[1]) have shown, is not a uniform body, but invariably consists of a mixture of several hydrocarbons, which can only be partially separated. For this reason the properties of the regenerated sylvestrenes also differ.

Haworth and Perkin[2]), when resolving a synthetically-prepared *l*-sylvestrene hydrochloride, m. p. 70 to 72°; sp. rot. α_D — 21,8°, with diethyl aniline, obtained a *l*-sylvestrene possessing the following characters: b. p. 176 to 178°, $d_{19°}$ 0,848, α_D — 68,2°, n_D 1,4761.

In order to obtain irrefragable proof that the terpene which occurs in the oil of *Dacryodes hexandra* is in effect *l*-sylvestrene, we mixed the *l*-hydrochloride, m. p. 68°, obtained from it with an equal quantity of *d*-sylvestrene hydrochloride, m. p. 71°, and crystallised it from methyl alcohol. The result was an inactive carvestrene hydrochloride, melting sharply at 52°. Thus the presence of *l*-sylvestrene in this oil, which was only rendered probable by the investigations of A. More, is now proved beyond doubt.

Elecampane Oil. We have just worked up an excellent parcel of root, rich in oil, and we are therefore again able to supply new oil with a full helenine-content. We have been able to reduce the price of the newly-distilled oil somewhat.

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[1]) *Liebigs Annalen* **399** (1913), 156; *Report* October **1913**, 135. — [2]) *Journ. chem. Soc.* **104** (1913), 2234; See p. 132 of the present *Report*.

Oil of Eryngium fœtidum. We have already stated on a previous occasion[1]) that a solid acid has been discovered at Buitenzorg in the distillation-water of this oil. The most recent issue of the Year Book of the "Departement van Landbouw" states that the m. p. of this acid is from 165 to 166°. Quantities of the acid weighing 0,223 and 0,1705 grams neutralised respectively 13 and 10,1 cc. decinormal potash liquor, which corresponds to an acid value of 327,1 and 332,4 respectively[2]).

Essential Oils, Sicilian and Calabrian.

We are again indebted to our friend, Mr. Eduardo Jacob, of Messina, for a detailed report on the oils of the *agrumi*, which, in accordance with our practice, we quote in full: —

It appears from the statistical returns of the exports of Sicilian and Calabrian essential oils from the ports of Sicily and Calabria for the year 1913, that in respect of quantity the shipments during that year have fallen below those of 1912 by 97631 kilos, whereas on the other hand, notwithstanding the smallness of the weight shipped, the value of the essential oils exported in 1913 surpassed that of the preceding year by 1280728 *lire*. That is to say, there has been a decrease in the shipments by weight of about 11 p.c., and an increase by value of about 6 p.c.

The above figures are convincing evidence that the conditions of production in the winter from 1912 to 1913 have been unusually bad, and this fact explains both the smallness of the exports, and their high value. The increase in value of the essential oils, especially oil of lemon, was the more felt because no old stocks from the season 1911/12 had been carried over into the season 1912/13, and because in the year 1913 the trade had to depend entirely and solely upon the output of the current season. In view of the high prices, consumption has been restricted as far as possible, but this notwithstanding it was so large that towards the end of 1913 also, before the opening of the new season, all the stocks, here as well as abroad, were practically speaking entirely exhausted.

Bergamot Oil. At the beginning of September 1913, bergamot oil stood at the basis of approximately 47 ℳ, and at this price it remained until the beginning of December 1913. It was only when more plentiful supplies of the new oil were arriving on the market that the article began to fall, slowly but steadily, with the results that in the months from December to the end of February it sagged from 47 ℳ down to almost 37 ℳ. Different estimates of the new crop were formed, according to the appearance of the trees during the dry summer. Some thought very favourably of the prospects of the coming crop, others feared that the prolonged drought would injuriously affect the oil-content of the fruit. But in spite of the fact that towards the end of the summer a few excessively hot days damaged part of the young fruit and caused it to fall prematurely, the bergamots which had remained on the trees developed so favourably in the course of the autumn and the early winter months, that the crop, taking it all round, may be described as a very fair average indeed. Influenced by the favourably-sounding reports, foreign buyers in the course of the summer exhibited great scepticism with regard to the proposals for business for delivery made to them

[1]) Comp. *Report* October **1913**, 49. — [2]) *Jaarb. dep. Landb. in Ned.-Indië*, Batavia, **1912**, 57.

from this side. They adopted towards the high prices then demanded an attitude of masterly inactivity, which in fact, had the result intended, namely that the owners, in order to find purchasers for their wares, were compelled to reduce their prices steadily. These conditions continued to affect the market so long as manufacturing was brisk, and the quantities of new oil brought to market grew larger day by day. But when, at the beginning of the month of March 1914, manufacturing came to an end, the daily market-supply of course began to shrink, and those parcels of oil which still were available now remain in the hands of strong holders, who are not at all eager to sell, and whose custom it is, in most cases, to speculate with their holdings for awhile upon a possible bad outturn of the coming crop. In sympathy with this state of things it is possible that in the course of the next four or five months less bergamot oil than heretofore will be offered for sale in the market, and that consequently there is a possibility that for some period to come higher prices will rule. On the other hand, it is not possible to disregard the fact that artificial bergamot oil and the many substitutes for the natural article are becoming more and more popular among the consumers. The reason that, in spite of these disadvantages, bergamot oil continues to be able to maintain so high a level of prices compared with former years, is no doubt the steadily increasing consumption of this and similar oils throughout the world. If, at the critical period, the industries concerned had failed to find a substitute for the costly natural oil (which in fact they then did find), natural bergamot oil would be much dearer still than it is now. Taking it all round, its future course of values will be determined by the conditions of flowering of the trees which will prevail a few months hence. If the new flowering-season should awaken good expectations, the owners of available oil will be induced to realize it while they are still able to command acceptable prices; on the other hand, if the prospects of the coming crop should be bad, a wild speculative movement may be let loose in the producing districts. At present it is impossible to form any opinion of the prospects of the new crop one way or the other.

Lemon Oil. The position of this article in the month of September was as follows: Old prompt oil was held by the few local owners at about 32 ℳ to 33 ℳ, while the ruling price for new oil for delivery in January/March was approximately 24 ℳ to 25 ℳ. Foreign buyers purchased the new oil for delivery freely and eagerly, while holding off as much as possible from the old prompt high-priced article. They tried to the utmost to supply their immediate requirements from the existing stocks abroad, in the hope that an early commencement of the gathering-season would make it possible to replenish the empty warehouses as early as November and December with cheap supplies. The paucity of the demand for prompt oil finally compelled the holders of such oil to adjust their demands to the unfavourable market-conditions and to accept offers which grew steadily lower. On the other hand, the foreign demand for oil for future delivery continued brisk, for there was no disguising the prevalence of the impression that several factors were in existence which might well have the result of bringing about increased firmness in the prices of lemon oil. The most important of these was that no large accumulation of new supplies was to be expected before the spring; secondly, there was what seemed to be a well-founded hope that the export of green lemons, especially to the United States, would assume unusually large dimensions in the coming season. For it was known that the Californian lemon- and orange-plantations had been extensively damaged, both as to fruit and trees, by severe frosts in January 1913, and in addition to this, the reduction in duties decreed

by the new United States Customs Tariff last September had become operative with the new season. Rarely have expectations based upon a reduction in customs duties been more cruelly disappointed than in the case at issue. The great drought which prevailed here until far into December prevented the lemons from maturing at the proper time, and from being suitable for shipment as boxed fruit. Hence, quantities of fruit, which in ordinary circumstances would have been sent abroad boxed, remained on the trees, exposed to all the attacks of the various diseases to which the lemon-tree is subject, and became unfit for shipment. What little fruit was sent out boxed was not of absolutely sound quality and, in spite of the reduction in the tariff, failed to find a ready market in America on account of its defective quality. More and more the conviction gained ground that the major portion of the lemons for which a sale abroad in the green state had been anticipated, must remain in the country, to be turned into lemon oil or citrate of lime. Add to this that for some time the report was current that certain big speculators in Sicily would find themselves unable to take up the large parcels of oil for delivery they had booked, and it will be understood that the market fell a prey to an evergrowing want of confidence, accompanied by increased willingness to sell. A race to realize set in, not only on the part of the manufacturers, but also on that of many exporters, who, by always making cheap offers abroad and thus discounting afresh the possibility of further reductions in price, did their best to create a panic which was not warranted by the actual state of affairs, and thereby helped to depress the article far below its intrinsic value. Thus it happened that oil of lemon first gradually and slowly receded, in the months of October, November and December 1913, from 24 ℳ to 22 ℳ, and then, in the course of January and February, tumbled down to 17 ℳ. Naturally such a depreciation could not pass without inflicting serious losses upon the local manufacturers. Now, of course, the important question arose whether it was not possible to put a stop to this drop in prices, which appeared to be bottomless. Since then negotiations have been on foot among the manufacturers with the object of withholding a portion of the oil from the market for the present, by warehousing it and advancing money on it. The first attempts which were made in this direction have had the immediate effect of arresting the downward movement in oil of lemon, and of bringing about an improvement in prices. Local speculators, who had left the article to take care of itself during the slump, now believed that the moment had arrived to secure control of it again at the much lower prices now ruling; many exporters, who apparently had calculated upon still lower prices, turned their thoughts to the covering of some portion of their bear sales. The manufacturer drew fresh courage in the expectation of better times ahead, and the panic disappeared, giving place to a more hopeful feeling. In view of the fact that owing to the large number of manufacturers the negotiations would be attended with some difficulties, which it would be impossible to remove there and then, incurable price-cutters have during the last few days resumed their old tricks of discounting the downward movement and spoiling the market. This, unfortunately, will result in creating a false impression abroad of the position which exists here. There is no doubt that the negotiations which are in progress among the manufacturers will in the end lead to a tangible result, and that the market-position of oil of lemon will undergo an improvement within a short time. The exaggerated rumours of the abundance of the present season's output of oil, which are being bruited about by various interested parties, have probably only a slight foundation in truth. It is true, however, that the output of manufactured oil this year will exceed that of the previous season by from 25 to 35 p. c., but this surplus will scarcely have any practical weight,

Exports of Essential Oils in the year 1913.

Country of Destination	1912		1913	
	Kilos	Lire	Kilos	Lire
a) Messina:				
North German Ports	4 697	112 728	10 158	304 740
Austria-Hungary	54 710	1 313 040	44 968	1 349 040
Belgium	1 226	29 424	1 442	43 260
Denmark	600	14 400	1 540	46 200
France	48 462	1 163 088	40 265	1 207 950
Greece	—	—	—	—
United Kingdom	111 565	2 677 560	112 029	3 360 870
Netherlands	4 170	100 080	3 140	94 200
Russia	5 212	125 088	4 309	129 270
Sweden	952	22 848	800	24 000
Norway	75	1 800	40	1 200
Spain and Portugal	867	20 808	1 772	53 160
Turkey	—	—	40	1 200
United States of America	335 906	8 061 744	297 061	8 911 830
South America	5 677	136 248	548	16 440
Australia	20 430	490 320	14 279	428 370
Egypt	225	5 400	110	3 300
India	45	1 080	—	—
Italy	22 624	542 976	16 857	505 710
Other countries	250	6 000	680	20 400
Total	617 693	14 824 632	550 038	16 501 140
b) Catania:				
North German Ports	8 070	193 680	3 477	104 310
Austria-Hungary	8 475	203 400	4 437	133 110
Belgium	3 829	91 896	646	19 380
Denmark	1 481	35 544	446	13 380
France	9 301	223 224	3 600	108 000
Greece	—	—	—	—
United Kingdom	13 484	323 616	4 583	137 490
Netherlands	4 972	119 328	1 003	30 090
Russia	1 146	27 504	426	12 780
Sweden	349	8 376	380	11 400
Norway	—	—	40	1 200
Spain and Portugal	56	1 344	—	—
Turkey	—	—	445	13 350
United States of America	35 032	840 768	9 853	295 590
South America	430	10 320	418	12 540
Australia	3 530	84 720	3 720	111 600
Egypt	—	—	127	3 810
India	—	—	—	—
Italy	30	720	—	—
Other countries	370	8 880	392	11 760
Total	90 555	2 173 320	33 993	1 019 790

Country of Destination	1912		1913	
	Kilos	Lire	Kilos	Lire
c) Reggio (Calabria):				
North German Ports	7 533	263 655	12 283	429 905
Austria-Hungary	8 914	311 990	1 058	37 030
France	31 069	1 087 415	24 891	871 185
United Kingdom	350	12 250	307	10 745
Netherlands	—	—	—	—
United States of America	16 795	587 825	5 109	178 815
Other countries	1 034	36 190	3 657	127 995
Total	65 695	2 299 325	47 305	1 655 675
d) Palermo:				
North German Ports	3 338	66 760	5 606	140 150
Austria-Hungary	11 286	225 720	18 062	451 550
Belgium	885	17 700	1 680	42 000
Denmark	125	2 500	40	1 000
France	3 615	72 300	7 396	184 900
Greece	—	—	21	525
United Kingdom	22 317	446 340	33 115	827 875
Netherlands	515	10 300	435	10 875
Russia	—	—	105	2 625
Sweden	—	—	—	—
Norway	—	—	—	—
Spain and Portugal	—	—	—	—
Turkey	20	400	131	3 275
United States of America	12 919	258 380	33 740	843 500
South America	—	—	—	—
Australia	380	7 600	45	1 125
Egypt	—	—	—	—
India	—	—	—	—
Italy	—	—	—	—
Other countries	—	—	—	—
Total	55 400	1 108 000	100 376	2 509 400

Total Exports in 1913.

Port of shipment	1912		1913	
	Kilos	Lire	Kilos	Lire
Messina	617 693	14 824 632	550 038	16 501 140
Catania	90 555	2 173 320	33 993	1 019 790
Reggio (Calabria)	65 695	2 299 325	47 305	1 655 675
Palermo	55 400	1 108 000	100 376	2 509 400
Total	829 343	20 405 277	731 712	21 686 005

1913 . . . . Kilos 731 712 . . . . . Lire 21 686 005
1912 . . . . „ 829 343 . . . . . „ 20 405 277
1913 decrease Kilos 97 631 . . increase Lire 1 280 728

— about 11 p.c. by weight. + about 6 p.c. by value.

seeing that last year the supplies in the consuming countries were drained dry, down to the smallest stock of the smallest consumer. The subsequent course of the lemon oil market during the second half-year of the present season will be determined in the last resort by the prospects of the new crop, which it will be possible to estimate to some degree about the month of June. A favourable development of the young flowers and a plentiful and healthy setting of the new fruit will have a depressing effect upon the market for "prompt" oil, whereas poor flowering and climatic conditions adverse to the setting of the fruit will stiffen the price of this season's oil.

Mandarin Oil. The crop is small, but so is the demand. The price of this oil has fluctuated several times between 40 ℳ and 35 ℳ.

Orange Oil, bitter. In September of last year the quotation stood at the very high level of 31 ℳ to 32 ℳ, the stocks having shrunk to an unprecedented extent. In spite of small arrivals, however, the price of this oil has dropped in the course of the autumn and winter down to 23 ℳ, as a result of the poor demand, and at this figure it is now to be had. It is probable that in the course of the next six months an improved demand will set in for this oil and that, as a result, the price will advance again.

Orange Oil, sweet. In September of last year the basis price for old sweet orange oil was about 30 ℳ, and the approximate price paid for new oil for early delivery was 27 ℳ. The prospects of the crop and the manufacture were not good, and gave no reason for suspecting any serious fall in the price of the oil. Nevertheless, no sooner had the new oil made its appearance than prices began to recede seriously, the principal reason of this state of things being one of serious portent for the essential oil industry of Sicily and Calabria, namely the appearance of a powerful competitor in the shape of West Indian orange oil, the quality of which is reported to equal that of very fair average Sicilian oil. Sweet orange oil has in the past been a favourite object of local speculation, because the quantity produced is relatively small, and the chances of making an easy profit are considerable. The appearance upon the market of a new source of production has had a paralysing effect upon the local love of speculation, and so the article has been left to itself, that is to say to the natural play of supply and demand. Thus it happened that in spite of the really very poor output the value of the oil fell in the course of the months of October to February from 27 ℳ down to 24 ℳ and still less, the fall being only interrupted by a few weeks of slight improvement in the closing days of December and the beginning of January. It is scarcely to be expected that there is any chance of considerable upward movements in this oil in the future, in particular because the world's consumption of it appears to be growing steadily less. The stocks now existing in this country are not important, and certainly smaller than those at the corresponding period of last year.

Lemon Oil. Dr. C. Kleber, of Passaic, N. J., gives us the following information with regard to the citral-content which has lately been observed in oil of lemon.

In former years the normal citral content of oil of lemon was from 4,3 to 4,8 p.c., but such oils are nowadays very rarely found in commerce. By far the great majority of the samples of lemon oil which now come under our observation only shew citral-

contents of from 3,5 to 3,9 p.c. (phenylhydrazine method). As the U. S. Pharmacopœia lays down 4 p. c. as the minimum limit of value, this circumstance often leads to disagreeable controversies with the Government officials. It is difficult to determine whether the low citral-content is due to abnormal conditions of the crop, or whether, perhaps, owing to the prevailing scarcity of oil, large quantities of distilled oils with a low citral content, or even terpenes, have found their way into commerce.

We may add to the above that we have found guaranteed genuine oils to contain from 3,8 up to 5 p.c. of citral (phenylhydrazine method), but that lately the content has usually been about 4 p.c. Our previous statement (*Report* October **1911**, 45) that the citral content of lemon oil ranges from about 4 to 5 p.c. may therefore be regarded as correct. At any rate a sample which is otherwise above reproach should not be rejected because its citral-content falls a little below 4 p.c. The U. S. Pharmacopœia should take this fact into consideration.

A method for the estimation of the hydrocarbon-content of concentrated lemon oils has been worked out by E. Böcker[1]), who had already on a previous occasion published a paper on terpene- and sesquiterpene-less oils[2]). His method consists in first abstracting the citral from the oil by means of sodium sulphite, and then removing from it the remaining aromatic substances by washing-out with alcohol of which the strength has been expressly so selected, that, provided certain precautions are observed, the hydrocarbons remain almost entirely undissolved. Böcker proceeds as follows: —

By the sulphite method the citral content is first estimated, 10 cc. of oil being used. When the oil which has not entered into reaction is less than 6 cc., the estimation is repeated either with 5 or with 10 cc. The unattacked oil left over from the two tests is put together, and 5 cc. of this citral-free oil is placed in a separating funnel of 600 to 700 cc. capacity in which, immediately previously, 500 cc. of spirit of precisely 51 p. c. by volume, cooled down to from 0 to — 2°, has been introduced. The separating funnel is closed with a cork and the contents are repeatedly shaken, by which manipulation the aromatic bodies of the oil are absorbed by the alcohol, while the hydrocarbons are left behind almost quantitatively. The separating funnel is then placed in a cooling-bath of 0°, cork downwards, and left there from 6 to 10 hours. It is then taken out of the freezing-mixture, carefully turned back to its proper position and placed in a stand. When the alcoholic solution has cleared to a point at which only a slight film remains (which in certain conditions may take up to 2 days) it is drawn off to about 10 cc., any oil-drops which may still adhere to the sides of the funnel being rinsed down with ice-cold 50 p. c. (51 p. c.?) alcohol, so that all the oil which has remained undissolved is brought together. When the mixture has become perfectly clear, the oil, being freed as far as possible from the last traces of alcoholic solution, is transferred to a measuring tube calibrated to $^1/_{10}$ cc., and the vessel rinsed out with a little more ice-cold 51 p. c. alcohol. It is advisable to use a separating funnel of which the lower part ends in a narrow, graduated tube. As soon as the oil is completely cleared (when the froth is very persistent a few drops of dilute acetic acid should be added), the volume is read off, calculated as original oil, and expressed in percentage-proportions.

When a sufficient quantity of material is available, the method may be completed by estimating not only the quantity but also the character and the properties of the

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[1]) *Journ. f. prakt. Chem.* II. **89** (1914), 199. — [2]) *Ibidem* II. **81** (1910), 266; *Report* April **1910**, 152.

eliminated hydrocarbons. Böcker prescribes the following *modus operandi:* from 100 to 200 cc. of oil is fractionally distilled *in vacuo.* The distillation is only continued up to the point where the separate fractions of about 10 cc. each still show dextrorotation. These fractions are put together as the "terpene-containing portion" of the oil, the rest constituting the "sesquiterpene-containing portion". Each of these portions is then freed from citral by means of sodium sulphite, and in both cases the residue is treated with 100 times its quantity of ice-cold 51 p. c. alcohol in the manner detailed above, a large glass flask being, if necessary, substituted for the funnel. The alcoholic solution is separated by means of a syphon from the portion which has remained undissolved. The oils which have been separated are estimated quantitatively, and from the values thus obtained the percentage-proportion of terpenes and sesquiterpenes in the original oil is calculated. For purposes of further identification the rotation is estimated, and, if necessary, the characteristic derivatives are prepared. The terpenes, of which the principal constituent is *d*-limonene, are characterised by a pronounced dextrorotation; they yield a liberal proportion of limonene tetrabromide, whereas the sesquiterpenes, which consist chiefly of bisabolene, are lævorotatory and may be identified from the bisabolene trihydrochloride.

Böcker has tested his method successfully with a whole series of experimental mixtures. In the case of a terpeneless lemon oil of his own manufacture he found 51,5 p. c. citral and 21 p. c. hydrocarbons; another sample of the same description, free from terpenes and sesquiterpenes, gave 62 p. c. citral and imponderable traces of hydrocarbons. For terpeneless lemon oil, Böcker considers a hydrocarbon percentage of 25 to 30 to be normal. He assumes that the hydrocarbon content of other concentrated essential oils may be estimated in a similar manner and is engaged in experiments on the subject.

It is familiar ground that the terpeneless lemon oils are differentiated in those which have been freed from terpenes only, and those which have also been freed from sesquiterpenes. Moreover, according to the different methods of treatment, which are kept secret by the various manufacturers, the elimination of hydrocarbons is more or less complete, hence the characters of the resulting oils exhibit somewhat considerable divergences. E. J. Parry[1]), who has examined a series of such concentrated lemon oils, has observed the following limits of value:—

	Terpeneless	Terpene- and sesquiterpeneless
$d_{15°}$ . .	0,8935 to 0,899	0,898 to 0,902
α_D . .	$-5°$ to $-8°30'$	$+1°$ to $-3°45'$
n_D . .	about 1,4810	—
Citral .	42 bis 48 %	average 65 % or a little more.

The terpeneless oils did not contain above 5 p. c. of terpenes; generally the proportion was even less than that. A higher terpene-content is expressed by a reduction of solubility and a lower specific gravity. Moreover, the lævoration diminishes, and, where this is possible, is converted into dextrorotation. The particulars given of terpene- and sesquiterpeneless oils refer to preparations in which little or no hydrocarbons were left.

In connection with the above, Parry further observes that although it is true that the solubility of lemon oil is increased in proportion to the degree of completeness

[1]) *Chemist and Druggist* **83** (1913), 378.

of elimination of the hydrocarbons, this is only achieved at the expense of the aroma, which, properly speaking, ought not to be sacrificed to solubility. For this reason Parry prefers the ordinary terpeneless lemon oil to that which has been freed both from terpenes and from sesquiterpenes.

Eucalyptus Oil. The advance in price to which we referred in our last *Report*, and which was the outcome of the shrinkage of the previously large stocks held on the European markets, has brought about a persistent animation in the trade in Globulus-oil with a high percentage of eucalyptol. Large parcels changed hands at rising prices, because the pressure was removed which had previously been exerted upon the market by the existence of large supplies, especially in London. Only quite lately has the tone become a little quieter, as the result of a few large arrivals from Australia, which proved, notwithstanding the high prices realized by them, that no shortage of oil is to be feared, in spite of the assertions of certain speculators. The quality of these newly-arrived parcels was satisfactory throughout; they contained, in part, over 85 p.c. of eucalyptol. The ordinary Australian oil of Amygdalina-character has undergone no alterations in price whatever; the supplies are equal to the demand.

We gather from the annual report of the Biological-Agricultural Institute at Amani for 1st April 1912 to 31st March 1913[1]) that of all the eucalypts planted there, *Eucalyptus citriodora*, *E. maculata*, *E. resinifera* and *E. amygdalina* have made the finest growth. *E. corymbosa*, *E. robusta*, *E. goniocalyx*, *E. microcorys*, *E. paniculata*, *E. rostrata*, *E. meliodora*, *E. salubris* and *E. pilularis*, also made good wood.

J. Elgart[2]) has made a control-test of Milne's method of eucalyptus treatment[3]) for scarlatina and measles, which consists in rubbing the whole body of the patient at the beginning of the illness with eucalyptus oil. Elgart found this treatment to be extraordinarily suitable as a prophylactic in scarlatina and measles. It reduces the mortality as well as the number of serious complications. Elgart has modified Milne's method by concentrating the therapeutic treatment upon the disinfection of the breathing-passages, the gate of the entry of the disease. He recommends a combination of the two methods.

In the year 1913 Parts 8 and 9 of the second volume of J. H. Maiden's exhaustive work "*A critical revision of the genus Eucalyptus*"[4]) have made their appearance. In these two parts the following species are described: *Eucalyptus macrocarpa*, Hook., *E. Preissiana*, Schauer (*E. pluriloculariis*, F. v. M.), *E. megacarpa*, F. v. M., *E. Globulus*, Labill. (*E. cordata*, Miq.; *E. diversifolia*, Miq.; *E. gigantea*, Dehnh.), *E. g.* var. *coronifera*, F. v. M., *E. Maideni*, F. v. M. (*E. Mortoniana*, Kinn.), *E. urnigera*, Hook. f. (*E. Whittinghamiensis*, Hort.), *E. u.* var. *elongata*, Rodway, *E. goniocalyx*, F. v. M., *E. g.* var. *acuminata*, Benth., *E. g.* var. *pallens*, *E. nitens*, nov. spec. (*E. goniocalyx* var. *nitens*, Deane et Maiden), *E. elæophora*, F. v. M. (*E. goniocalyx* var. *pallens*, Benth.; *E. Cambagei*, Deane et Maiden), *E. cordata*, Labill. and *E. angustissima*, F. v. M.

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[1]) *Der Pflanzer* **10** (1914), 54. — [2]) *Med. Klinik* **9** (1913), 1251; *Therap. Monatsh.* **27** (1913), 807. — [3]) Comp. *Report* April **1911**, 73. — [4]) Comp. *Report* October **1913**, 60.

Fennel Oil. In our last *Report* we described the outlook of the fennel market as favourable, because as a matter of fact several reports had been received which agreed in forecasting a plentiful output. The further development of affairs, however, has brought a tremendous disappointment, for whereas on the one hand the final result in the Russian producing districts had been over-estimated, it was further discovered that the oil-content of the new season's fennel was surprisingly small. As the weather at the ripening was favourable, the above deficiency can only have been caused by the unfavourable climatic conditions of the summer, during the period of the development and flowering of the plants. The samples examined by us showed a shortage in oil-content of 25 p.c. as compared with normal years, although the appearance of the fennel itself was not bad. Naturally, this unfavourable result soon made itself felt in increased prices of all classes of fennel oil, and those who, like ourselves, have to supply a large number of important and regular buyers in the confectionery trade were compelled to handle their stocks with economy. As practically no fennel has been offering lately, and as the Galician manufacturers of crude fennel oil are also extremely reserved in making offers, the fennel oil prices remain very firm, and in the course of the summer may well attain a level approaching that of anethol and leaving scarcely any advantage compared with the latter. In any case, fennel oil is one of the few articles in our branch of trade for which on this occasion we are able to predict higher prices.

Frankincense Oil. The frankincense oils (olibanum oils) found in commerce at the present time differ from those that have been examined by us in the past[1]) in being dextrorotatory. The rotation of the earlier oils ranged from α_D — 11 to — 17°, but latterly samples have come into our hands which showed α_D + 17° to + 29° 41′; the sp. gr., however, was the same as before. We were interested in discovering whether this difference in optical rotation was attended by any change in the composition of the oil. Our investigation was restricted to the terpene fractions of the oil, seeing that the non-terpenes had only quite recently been investigated by Fromm.

Gildemeister and Hoffmann, in *The Volatile Oils* 1st Ed., p. 590, name pinene, dipentene and phellandrene as constituents of olibanum oil. Pinene has been isolated from the oil by Wallach[2]), who showed it to be identical with Kurbatov's olibene. Wallach also found that the fraction boiling between 177 and 179° contained dipentene. The presence of phellandrene was established by Schimmel & Co. by the nitrite-test, in which connection it is a noteworthy fact that the oil, even before fractionation, responded to the phellandrene-test.

The oil now examined by us had the following constants: $d_{15°}$ 0,8775, α_D + 19° 18′, $n_{D20°}$ 1,47245, acid v. 1,8, ester v. 7,5, ester v. after acet. 106,0, soluble in up to 2 vols of 90 p.c. alcohol, the solution being clear at first, and turning turbid after 2 vols. Of the terpenes, 92 p.c. boiled between 156 and 161°, about 5 p.c. between 161 and 163°, and about 4 p.c. between 163 and 181°. In the fractions boiling between 156 and 157° ($d_{15°}$ 0,862 to 0,863; α_D + 30° 58′) we established the presence of *i*- and *d*-α-pinene from the nitrosochloride and the nitrol piperidide (m.p. 118°), as well as by oxidation into pinonic acid (b.p. 170 to 175° at 7 mm.; m.p. of the active acid 69 to 70°; of the inactive acid 104°). The presence of camphene in all the fractions boiling between 158 and 164° was established by conversion into *iso*borneol, m.p. 210 to 211°. Dipentene

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[1]) Gildemeister and Hoffmann, *the Volatile oils.* 1st Ed. p. 489. — [2]) *Liebigs Annalen* **252** (1889), 100; *Bericht* October **1889**, 37.

was identified from the tetrabromide, m.p. 124°, and *p*-cymene by treating the ultimate fraction with permanganate (*p*-hydroxy*iso*propyl benzoic acid, m.p. 156°). *β*-Pinene, phellandrene, and terpinene could not be detected.

The terpene-fraction of dextrorotatory olibanum oil is therefore likewise dextrorotatory, and consists to the extent of nearly 99 p.c. of *α*-pinene and camphene; dipentene and *p*-cymene only occurring in the oil in very slight proportions (1 p.c.). Phellandrene, the presence of which in the earlier oil had been established by Schimmel & Co. was absent from the sample now under review.

In the high boiling fractions of oil of frankincense [b. p. 70° (12 mm.); $d_{15°}$ 0,9685; $\alpha_D + 20° 48'$], E. Fromm and E. Autin[1]) have discovered a body $C_{10}H_{16}O$, which boils between 210 and 211°, and to which they have given the name of olibanol. Olibanol has the properties of an alcohol, and possibly also those of a ketone. This may be due to its being a mixture of two substances, or to the fact that it is capable of reacting in two tautomeric forms. When oxidised with potassium permanganate in aqueous solution, olibanol gives rise to a dibasic liquid acid $C_{10}H_{16}O_4$. So far nothing is known of the constitution of this acid. In addition, there is formed from olibanol, with separation of a carbon-atom, pinononic acid, $C_9H_{14}O_3$. Treatment with bromine liquor showed this substance to be in effect pinononic acid, bromoform and norpinic acid being formed. The pinononic acid was furthermore identified by preparing its oxime (m. p. 187°) and its semicarbazone (m. p. 209°). The structural formula of olibanol cannot be definitely drawn up, however, as the outcome of these results of oxidation.

From the oxidation-liquid of olibanol, *d*-borneol (m. p. 201 to 202°), was isolated, from which it may be assumed that oil of frankincense contains esterified borneol.

Galangal Oil. We have distilled a few small parcels of galangal root, but unfortunately we have had to pay such high prices for them that we are only able to list this oil, which has long been wanting, at a very high figure. In spite of this many of our customers are glad to be able to procure once more oil of the excellent quality supplied by us, after they have been compelled to make shift for so long with the sometimes very questionable oils supplied by certain other firms.

Garlic Oil. We stated on p. 81 of our *Report* of April 1912 that according to Manindra Nath Banerjee, quicksilver can be completely freed from lead by rubbing it in a mortar with garlic-juice, which effect is produced by the essential oil contained in the spice. The author has now published fuller details of this purification-method in another place[2]).

Geranium Oil. Now that the Algerian growers are hardly willing to sell their oil otherwise than by contract running over several years, it is becoming more and more difficult to report on the market-value of this article. There is no longer any genuine market-price for African geranium oil, for the large quantities which have been bought by certain speculators as an investment, continue to influence the market in an altogether irregular manner. Holders who happen to be in want of money sell cheaply as soon as they receive deliveries on account of their contracts, and when just at the moment no customer can be found, the oil is, in certain conditions, sold

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[1]) *Liebigs Annalen* **401** (1913), 253. — [2]) *Zeitschr. f. anorg. Chem.* **83** (1913), 113.

at a loss. Other factors have long ceased to determine the course of prices. Since is has become known that before long Morocco may be expected to supply large quantities of geranium oil a certain feeling of nervousness has seized the middlemen, most of whom have made contracts for several years ahead at firm and high prices, and occasionally we find that our customers are in receipt of quotations, even for moderate quantities, which indicate anxiety to sell as much as possible of the quantities contracted for at rates which will leave any profit at all. The reports of prospective or actual crop-failures which are spread from time to time have been unable to effect any change in the tendency, and the result is that it is possible at the present time to buy African geranium oil, according to the opinion held of the market by the speculator concerned, at practically any price. Naturally it is the consumers who profit by a state of things which is extremely disagreeable for the middlemen.

The exports of African geranium oil from Algeria have been as follows: —

1913	. . .	38400 kilos
1912	. . .	29900 „
1911	. . .	28500 „ .

Prices of Réunion geranium oil have suffered an enormous decline within the ast few months; in September 1913 the quotation was 70.— *fcs.*, whereas within the last few weeks some business has been done at 33.— *fcs.* The unsatisfactory condition of the African geranium oil market and the corresponding decrease in the demand for Réunion oil is probably the principal cause for this decline. The figure of 33.— *fcs.* appears, however, to have been regarded in a certain quarter as worthy of speculative operations, for we hear that a firm which has long made it its pride to disturb the market from time to time by special *coups* has bought up large quantities in Réunion at this price, and has thereby brought about a stiffening of the market. As the cyclone-season is said to have passed this time without causing damage to the plantations, this firmness will probably only be prolonged if the firm in question continues its purchases for a long time.

According to the Chamber of Commerce at St.-Denis, the exports of Réunion geranium oil in the year 1913 amounted to 37614 kilos, compared with 43138 kilos in the year 1912.

From an article by E. Charabot and C. L. Gatin[1]) on the cultivation of the geranium plant we cull the following particulars in amplification of our previous statements[2]).

According to the authors above named, several other species besides *Pelargonium graveolens,* Ait. are grown for purposes of geranium oil distillation.

On the Island of Réunion irrigation of the plants is practised. This, it is true, secures a more regular development, but on the other hand it reduces the oil-content of the plants. Crops are gathered on the island throughout the year; from 1000 to 1800 kilos of the herb are needed to produce 1 kilo of oil (= 0,56 to 0,1 p.c.) which equals a yield of from 30 to 50 kilos per hectare (= about $14^1/_2$ to 24 lbs. per acre).

In Réunion and in Algeria almost every plantation has its own still, a contrivance of very simple construction, with a false bottom.

In Algeria the preparation of geranium oil has fallen off very much in the course of the last few years. Charabot and Gatin ascribe this fact to the speculation which

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[1]) *Journ. d'Agriculture tropicale* **12** (1913), 289. — [2]) Comp. *Report* April **1907**, 54; October **1910**, 70; October **1913**, 61.

prevails in the wine-trade, and which has led to the substitution of vines for geranium in many localities.

In Réunion also the distillation of geranium oil has diminished. Speculators have taken advantage of this state of things by buying up large stocks of geranium oil, to the disadvantage of the perfumery industry and of the future of geranium-growing. The consequences have not failed to make themselves felt: the geranium oil prices have risen considerably, and the demand for substitutes such as geraniol and diphenylmethane has become very brisk.

On p. 63 of our last *Report* we referred to an article by E. M. Holmes on the scented *Pelargonium* species. Since then, a continuation of this article has been published[1]) in which Holmes gives further particulars of the aroma of numerous species and varieties of the genus *Pelargonium*.

On the citronellol-content of geranium oils, see p. 121 of the present *Report*.

Ginger Oil continues to be cheap, at unchanged prices, inasmuch as all varieties of ginger suitable for distillation have been plentiful.

A sample of ginger oil which has been investigated at Buitenzorg gave $\alpha_D + 13°9'$[2]). We have previously come across another sample of dextrorotatory ginger oil, which had been distilled from Japanese root[3]).

Gingergrass Oil. The prices have kept up well, for although the demand was slight, the arrivals were very small, and only just sufficient to cover the requirements. The article no longer appears to possess any great importance.

Guaiac Wood Oil. The oil distilled by us, which is distinguished by special purity of aroma, and which on that account is appreciated everywhere, has been continuously in brisk demand, but as there have been no difficulties in the way of procuring fresh raw material we have been able to maintain our low prices. As a matter of interest we may state that the last parcels of wood which have come to hand included logs weighing about 2 tons each. Such logs can be handled only by the most up-to-date and powerful reduction-plant, such as is, of course, at our disposal.

Oil of Helichrysum angustifolium. In our *Report* of October 1911, p. 54, we briefly described a sample of oil of *Helichrysum angustifolium*, DC. (N. O. *Compositæ*), derived from Dalmatia. Since then we have received from the same source two other samples of oil, of which we will also set forth the characters here, in view of the fact that little is as yet known of *Helichrysum* oil. One sample was pale brown, soluble in 8 to 9 vols. a. m. of 90 p. c. alcohol, and possessed the following characters: $d_{15°}$ 0,8923, α_D − 9° 40′, $n_{D20°}$ 1,48490, acid v. 2,8, ester v. 39,2, ester v. after acet. 65,8. The second sample gave the following values: $d_{15°}$ 0,8964, α_D — 9° 38′, $n_{D20°}$ 1,48422, acid v. 1,9, ester v. 56,2, soluble in 10 vols. a. m. of 90 p. c. alcohol.

Juniper Berry Oil. We have during the winter distilled large quantities of excellent Italian berries, which could be bought this season at more advantageous

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[1]) *Perfum. Record* **4** (1913) 372. — [2]) *Jaarb. dep. Landb. in Ned.-Indië*, Batavia, **1912**, 57. — [3]) See Gildemeister and Hoffmann, *Die ätherischen Öle*, 2nd Ed., Vol. II, p. 293.

prices than any other. Unfortunately our manufacturing was seriously interrupted by the destructive fire of 18th October last, when a large part of the berries was destroyed. The demand for oil of our own distilling is always so satisfactory that we are able to realize full prices. The position of the article may therefore at present be described as firm.

Oil of the Berries of Juniperus phœnicea. An oil distilled in the island of Cyprus[1]) from the immature berries of *Juniperus phœnicea*, L. was of a pale-yellow colour. It possessed the following characters: $d_{15^\circ}^{15^\circ}$ 0,8684, α_{D20° + 3° 4′, sap. v. 9,8, sap. v. after acet. 16,8, not clearly soluble in 10 vols. of 80 p. c. alcohol. With 9 vols. of 90 p. c. alcohol the oil makes a faintly opalescent solution.

We referred to a similar oil on p. 69 of our *Report* of April **1913**.

Laurel Oil. An oil of laurel leaves distilled in Cyprus has been examined at the Imperial Institute in London[2]) and found to possess the following characters: d_{15° 0,9224 to 0,940, α_D 4° 45′ to — 11° 32′, sol. in 1 to 1,7 vols. 80 p. c. and in 5 to 6 vols. 70 p. c. alcohol. The cineol-content of two samples was respectively 66 and 71 p. c. (resorcinol method).

We recorded similar characters for oil of Cyprian laurel leaves a few years ago[3]).

Lavender Oil. As already stated in our last *Report,* in spite of the bad crop of last summer, the large stocks which were carried over into the new season have prevented the continuance of the high prices which were demanded at the opening markets for lavender oil last September. A few buyers then paid as much as 40.— *frs.* and more per kilo for oil of good quality. But the withdrawal of these buyers from the market brought about a cessation of business; soon the sellers became more tractable, and since the close of the year it has been possible to buy a few parcels here and there at a few francs per kilo below the above-mentioned figure, according to quality. Unfortunately these parcels have all been small, and up to the present they have therefore been unable to influence seriously the general position of the market. Large quantities, however, still remain in the hands of the growers and the nearer draws the time of the new crop, the more anxious these will become to sell their holdings at a profit, as it is hardly to be expected that the coming summer's crop will again be a failure. But in our opinion it is scarcely likely that there will be any considerable fall in prices before the 1914 crop is due.

Since we have commenced the steam-distillation of lavender in our Barrême factory, and have moreover established steam-stills in several other parts where the finest flowers are grown, several Grasse firms have followed our example. Even some of the farmers living in these districts have put up steam-boilers; that is to say they have so rebuilt their antiquated apparatus that the rinsing of the charge by boiling water, which action has the peculiarity of saponifying part of the esters during the process of distillation, is obviated. By this method they are now able to produce more valuable oils with a higher ester-content, and, consequently, to realize better prices. As we have already repeatedly stated these oils of high-percentage are in part sparingly-soluble; we have met with oils containing 40 p.c. ester which, although guaranteed pure, were only imperfectly soluble in 70 p.c. alcohol[4]).

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[1]) *Bull. Imp. Inst.* **11** (1913), 428. — [2]) *Ibidem* **11** (1913), 430. — [3]) *Report* April **1909**, 60. — [4]) See *Report* April **1907**, 66.

Lemongrass Oil. In spite of the briskness of the demand there has only been little change in the prices in India; they ranged with slight fluctuations between 2 1/8 to 2 1/4 d. p. oz., and were therefore a little below the quotations of last September. The production must therefore have been unusually large, for it is obvious that the perfumery industry did not allow the opportunity of making cheap purchases to pass by. Buyers everywhere appear to have laid in plentiful supplies and it is therefore not beyond the range of possibility that in the course of the summer a further slight decline may manifest itself.

The shipments from Cochin in the year 1913 have been as follows: —

Port of Destination	Quantity 1912	1913
London	17 737,5 lbs.	35 541 lbs.
Liverpool	—	9 223,5 „
Havre	54 450 „	50 605,5 „
Marseilles	102 432 „	140 431,5 „
Amsterdam	—	3 019,5 „
Antwerp	—	4 389 „
Bremen	2 194,5 „	8 844 „
Hamburg	48 246 „	71 247 „
New York	23 826 „	19 948,5 „
Total	248 886 lbs.	343 249,5 lbs.

We would seize this opportunity to call attention once more to a matter which we first ventilated many years ago, but which nevertheless appears to have been lost sight of. In our view it is altogether out of harmony with the present-day tendency towards simplification of our commercial system to continue to quote by the "ounce" an article such as lemongrass oil, which during the past few decades has attained a previously undreamt-of commercial importance, and of which the annual production now exceeds a quarter of a million pounds. If the British Board of Trade, which may be regarded as the leading authority in questions of this kind, were to take steps that would result in the abolition of this out-of-date practice it would earn the general approval of those concerned. The same thing applies to palmarosa oil, although a few firms who take a leading part in the trade in this oil have already succeeded in bringing about some improvement by invariably calculating their offers in "lbs.". Even although the United Kingdom and the rest of the British Empire may not be disposed to adopt the metric system, care should at least be taken not to render international traffic still more difficult by clinging to units of weight that are antiquated in the sense of being out of harmony with present-day needs. It should be possible to introduce in the lemongrass and palmarosa oil trade a practice which has been in existence in the citronella oil business for the past 25 years.

From the Société des Plantations de Kaoéni in Marseilles we have received a sample of lemongrass oil distilled in the island of Mayotte. Its specific gravity was 0,8933 (15°), opt. rot. — 0° 23′, and, in common with other oils of the same origin previously referred to[1]), it belonged to the group of sparingly-soluble lemongrass oils,

[1]) *Report* April **1913**, 72; October **1913**, 69.

for even in 90 p. c. alcohol it only gave a clear solution at first. The citral-content was found to be 87 p. c. when estimated with bisulphite, and 81 p. c. with neutral sulphite, and was therefore higher than in the previously-examined oils, which only contained from 73 to 78 p. c.

Remarkably enough, of three samples of Seychelles-lemongrass oil, which were sent to us from another quarter, one was readily and the two others sparingly soluble. From this circumstance it would almost appear as if both species of lemongrass occurred in the Seychelles, for as is well-known, the difference in the solubility of the oils is said to be connected with the parent-plant from which they are derived, *Cympobogon flexuosus,* Stapf yielding a readily-soluble, and *C. citratus,* Stapf a sparingly-soluble oil[1]). We are of course unable to say whether this assumption is well-founded in the case under review, or whether the difference in solubility is determined by other causes.

The characters of the Seychelles oils were as follows:—

			Aldehyde content		
$d_{15°}$	α_D	$n_{D20°}$	Bisulphite method	Sulphite method	
0,8954	— 0° 15′	1,48905	79 %	76 %	Sol. in 90 p. c. alcohol up to 2 vols. afterwards opalescence.
0,9101	— 0° 25′	1,49240	77 %	70 %	Sol. in 90 p. c. alcohol up to 4 vols. afterwards opalescence.
0,9008	— 2° 40′	—	86 %	81 %	Sol. in 2,3 vols. a. m. 70 p. c. alcohol.

Oil from Lignum nephriticum. On p. 69 of our last *Report* we referred to a paper by H. J. Möller on *Lignum nephriticum,* in which it was stated that, in the opinion of the author, this oil was the product of certain species of *Pterocarpus.* According to J. Small[2]), this is not correct; the parent plant of the drug being *Eysenhardtia amorphoides,* H. B. et K., N. O. *Leguminosæ.* Small bases his assertion upon a careful microscopical examination of the material, and upon a test of the aqueous extract of the wood. He further points out that some years ago Stapf[3]), as the result of a thorough examination of *Lignum nephriticum,* arrived at the same conclusion; but that Möller's paper contains no mention to Stapf's investigation.

Lime Oil. The sale of this oil has of course been affected unfavourably by the fall in the lemon oil market, but in spite of this a return to the old low prices is for the present out of the question. Very little hand-pressed oil has been received from the West Indies, and until the supplies increase the present level of prices is likely to be maintained.

The official organ of the Imperial Department of Agriculture for the West Indies, the *Agricultural News,* a paper published in Barbados, recommends that, as a protection for the young lime-plantations against the strong winds which prevail in the island of St. Lucia[4]), trees should be planted[5]). It is said that *Eucalyptus paniculata*[6]) is particularly suitable for this purpose. The trees should be planted before, and not after, the lime-plantations are laid down. In St. Lucia the lime industry increases year by year, but it is still second to the sugar industry.

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[1]) Comp. *Report* April **1907**, 33. — [2]) *Pharmaceutical Journ.* **92** (1914), 4. — [3]) *Kew Bull.* **1909**, 293. Small's paper erroneously gives the year as 1908. — [4]) Comp. *Report* October **1913**, 70. — [5]) *The Chemist and Druggist* **84** (1914), 304. — [6]) According to Baker and Smith (*A research on the Eucalypts,* Sydney 1902, p. 64) *E. paniculata,* Sm. occasionally grows to a considerable height.

Lime Leaf Oil. A sample of lime leaf oil received by the Imperial Institute in London[1]) from Montserrat showed the following characters: $d_{15°}^{15°}$ 0,8772, α_D + 38° 17′, sap. v. 27,6, sol. in 90 p. c. alcohol. Upon the addition of 9 vols. of the solvent opalescence ensued; 43 p. c. of the oil reacted with bisulphite solution.

Linaloe Oil. It might have been expected that the conditions prevailing in Mexico would have exercised more influence upon the course of prices than has in fact been the case, but the demand in Europe has only been slight, principally because owing to the drop of bergamot oil prices the need for bergamot substitutes, such as linalyl acetate etc., has diminished, and also because large supplies of excellent Cayenne linaloe oil are still available for the use of the perfume industry. The prices of the last-named variety also have not risen as much as would have been expected judging by the conditions which ruled last autumn. We hear that in Cayenne a bitter rivalry for the purchase of linaloe wood is in progress, which has caused prices to advance to a level at which the distillers must certainly prepare themselves for serious disappointments if European buyers should continue to refuse to concede the increased demands. The future course of the bergamot oil market will be the deciding factor in this question. Mexican oil was last offered at 25.— ℳ per kilo, Cayenne oil at 34.— *fcs.;* the first-named is therefore much too dear in proportion, and this explains the slowness of its sale.

For Shiu oil see p. 92 of the present *Report.*

Lovage Oil. As was to be anticipated, there has been a serious decline in the price of this article, the crop in Thuringia having been not only plentiful, but having degenerated into over-production, as a result of which the root has become completely depreciated. As there is only a limited sale for lovage oil the farmers have derived small satisfaction from their crop. We have been able considerably to reduce our price for 1913 oil.

Mastix Oil. This oil, which is largely used in the manufacture of beverages throughout the Orient, has been in greater demand than ever during the last few months, because the raw material could only be procured with difficulty, and at prices compared with which our quotations appeared at times to be very moderate indeed. We are about to distil another parcel, but it will depend upon the calculation of the result whether we shall be able to offer the newly-distilled oil at the present prices.

Mastix Leaf Oil. The oil[2]) prepared from the leaves of the Mastix tree *(Pistacia Lentiscus,* L., N. O. *Anacardiaceæ)* possesses the following characters: d 0,887, α_D + 3°. The oil contains 5,8 p. c. esters and 13,5 p. c. acetylisable constituents, as well as pinene and presumably also other terpenes and sesquiterpenes. Its aroma reminds of the oils of rue and of savin.

Oil of Mentha sylvestris. At the Imperial Institute in London[3]) an oil distilled in Cyprus, it is said from the herb of *Mentha sylvestris*[4]), has been found to possess the following characters: $d_{15°}^{15°}$ 0,9687, α_D + 31° 58′, sap. v. 24,9, sap. v. after acet. 175,5, sol. in 2,5 vols. a. m. of 70 p. c. alcohol.

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[1]) *Bull. Imp. Inst.* **11** (1913), 436. Comp. *Report* October **1906**, 79. — [2]) *Perfum. Record* **4** (1913), 403. — [3]) *Bull. Imp. Inst.* **11** (1913), 432. — [4]) Comp. *Report* April **1913**, 74.

Mustard Oil. We would not omit to point out that according to A. Schwarz[1]) mustard oil is an effective remedy in toothache and ear-ache. In the case of a patient who is suffering from toothache as a result of carious teeth, if a vial of about 20 gr. capacity containing about 5 gr. of essential oil of mustard, is held to the nostril, the patient told to shut his mouth and eyes and to smell once (that is to say, simply to inhale air once through the open nostril, the other nostril being lightly closed), the toothache disappears immediately. It is said that the oil also acts upon the first branch of the trigeminus, and is therefore effective in ear-ache.

Myrtle Oil. At the Imperial Institute in London[2]) a myrtle oil from Cyprus (derived from *Myrtus communis,* L.) has been found to possess the following characters: $d_{15^\circ}^{15^\circ}$ 0,9166 and 0,9302, $\alpha_D + 8^\circ 14'$ and $+ 8^\circ$, sap. v. 25,1, sap. v. after acet. 61,5, sol. in 5 vols. a. m. of 70 p. c. alcohol.

Neroli Oil. The new orange-flower crop will be belated this year, because cold weather has prevailed in the South of France during the months of January and February, with the result that at the time of writing (middle of March) the trees are barely beginning to show the first signs of new buds. It is therefore quite impossible at the present time to make any forecast of the result of the crop which, in normal conditions, is usually gathered between the end of April and the beginning of June, but which this year will be considerably delayed. Although the trees had to stand severe cold in the winter they do not appear to have suffered particularly, for happily the frost only hurts them when it follows hard upon rain, and they are only slightly sensitive to dry cold, such as prevailed last winter. It would therefore seem warranted to predict a normal yield of flowers were it not that, contrary to their usual habit, the orange trees blossomed last autumn in over-profusion, and that experience shows that such an excess of autumn-blossom causes a weakening of the whole organism of the tree, and is bound to result in a diminution of the principal blossoming this year. At present, therefore, the feeling in the South is that only a poor average crop is to be expected. The extent of the autumn-crop of 1913 may be gauged from the fact that the Société coopérative des propriétaires etc. received delivery of not less than 230000 kilos of flowers, whereas the quantity produced in the autumn of 1912 was only from 30 to at most 35000 kilos. Although the autumn flowers contain less oil than do those gathered in the spring, they were sold to the distillers at the same price as the latter, namely 55 centimes per kilo. The demand for genuine neroli oil has been pretty well sustained, for the Société coopérative, which had 531 kilos of oil distilled by itself in stock at the close of 1912, has not only sold this oil, but 80 kilos prepared in the spring of 1913 as well. The market, therefore, may be described as firm. It is to be hoped that the Société coopérative will come to an agreement with the Syndicate of Perfumers, in order that the owners of orange trees may get a somewhat more remunerative price for their flowers, for at 50 centimes a kilo (the price of 55 centimes paid by the distillers included carriage and commission), the cultivation cannot pay, and does not cover the cost of tending the trees and collecting the flowers. In consideration of the low price the Société coopérative has sold the whole of the 1617903 kilos of flowers received by it, with the exception of 84516 kilos which it has worked up itself. In previous years the quantity of flowers distilled by the Society was five to six times as large.

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[1]) *Münch. med. Wochenschr.* **1914**, 420; *Apotheker Ztg.* **29** (1914), 188. — [2]) *Bull. Imp. Inst.* **11** (1913), 433. Comp. *Report* April **1910**, 78.

The Deputy for the Constituency of Cannes-Antibes, which is the principal orange-flower producing district, has brought a Bill before the Chamber of Deputies imposing high customs duties upon foreign neroli oil and upon petitgrain oil, namely 100.— *fcs.* per kilo on the former, and 25.— *fcs.* upon the latter. The argument in favour of the proposal is that the foreign oils are inferior in quality to the French, and are used to adulterate, and as a substitute for, the latter. The Commission of Customs has decided to reduce the proposed duties to 70.— *fcs.* for neroli oil and 5.— *frs.* for petitgrain oil, and, thus amended, the Bill is shortly to come before the Chamber.

In the year 1902 we detected in our laboratory the presence in neroli oil[1]) of the following: *l*-α-pinene, camphene, dipentene, *l*-linalool, decylic aldehyde, phenyl-ethyl alcohol, *d*-terpineol, jasmone (?), phenylacetic acid, and benzoic acid. Shortly afterwards Hesse and Zeitschel[2]) reported on their investigation of neroli oil, in the course of which they found camphene, *l*-linalool, linalyl acetate, *d*-terpineol, geraniol, and geranyl acetate, and, in addition to these, indol, nerol, and nerolidol. Among these constituents of neroli oil, Tiemann and Semmler[3] had already at an earlier date isolated *l*-linalool and its acetic ester.

When we had occasion recently to establish the occurrence of nerolidol and peruviol in Peru balsam oil, (see p. 81) and, with this object, to isolate pure nerolidol, we noticed that neroli oil contains still another constituent with a b. p. exceeding that of nerolidol. This body is farnesol. We isolated this sesquiterpene alcohol $C_{15}H_{26}O$ at 120° from those fractions of the oil which boil above 127° (4 to 5 mm.) by treating them with phthalic anhydride. Its physical characters, which were as follow: b. p. 140 to 141° (3 to 4 mm.), $d_{15°}$ 0,8934, $\alpha_D \pm 0°$, $n_{D20°}$ 1,48991, agreed with those recently recorded by M. Kerschbaum[4]) for farnesol from ambrette seed oil. The body was oxidised into farnesal with bichromate and sulphuric acid. The aldehyde regenerated from the bisulphite-compound afforded a semicarbazone with a very indefinite m. p. In the case of the material examined by us, which turned soft first, it was found to be between 127 and 132°, whereas Kerschbaum[4]) gives it as from 133 to 135°. We had very little material at our disposal, so that it was impossible further to purify the substance. The farnesol content of neroli oil probably does not exceed 2 p. c.

Niaouli Oil. As is well known this oil, which goes in France under the name of *gomenol*, is distilled in New Caledonia from the leaves of a species of *Melaleuca*. Although the therapeutical action of the oil does probably not differ from that of cajuput oil or eucalyptus oil, it nevertheless has found numerous friends among the manufacturers of medicinal specialities, and our increasing sales indicate that in the future the article may acquire increasing importance.

Nutmeg Oil. There has been a sufficient selection of those varieties of nutmegs which are suitable for distilling, and it has therefore not been necessary to carry out the advance in prices which was lately feared to be unavoidable. We regard a decline in the market as practically out of the question, and the present quotations therefore appear to offer an inducement to lay in a plentiful stock. We always have several thousand kilos in our warehouse and are therefore able to offer nutmeg oil at advantageous prices.

[1]) *Report* October **1902**, 54; April **1903**, 53. — [2]) *Journ. f. prakt. Chem.* II. **66** (1902), 481; *Report* April **1903**, 53. — [3]) *Berl. Berichte* **26** (1893), 2711. — [4]) *Berl. Berichte* **46** (1913), 1733; *Report* October **1913**, 140.

Oil of Ocimum canum. Some years ago E. Charabot[1]) described an oil said to have been distilled from *Ocimum canum,* Sims (*O. americanum,* L.), N. O. *Labiatæ,* which contained a fairly large proportion of *d*-camphor. A sample of oil received from Dabakala (Ivory Coast) by the firm of Roure-Bertrand Fils[2]) showed altogether different properties from the product examined by Charabot, and contained no camphor. As E. G. Camus had examined the herb from which the oil explored by Roure-Bertrand Fils was distilled, and had identified it as *O. canum,* it may be assumed that the *Ocimum* species which passed through Charabot's hands differed from the first-named.

At ordinary temperature the oil described by Roure-Bertrand Fils deposits needle-shaped crystals soon after its preparation. These crystals often attain a length of several centimeters. When the oil is slightly warmed by hand it forms a faintly yellow liquid, highly refractive of light, of the following characters: $d_{32°}$ 1,0330, $\alpha_{D30°} - 2° 30'$, acid v. 0, sap. v. 301,4, sol. in 2¼ vols. a. m. of 75 p. c. alcohol, and in any proportion in 80 p. c. alcohol. The solid substance had m. p. 35 to 37° and proved to be identical with methyl cinnamate. The acid which had been separated out from the saponification liquors had the same m. p. as cinnamic acid (133°). The saponification value of the oil indicates that the probable methyl cinnamate content was about 87 p. c. The non-saponifiable constituents of the oil appear to consist of strongly lævorotatory hydrocarbons.

A sample of oil which had been distilled at Grasse from African material (yield 0,65 p. c.) gave the same constants as the oil distilled on the Ivory Coast.

We also have recently examined an oil from *Ocimum canum* which had been sent to us from Central Africa. Its constants were as follow: $d_{30°}$ 1,0431, $\alpha_D - 2° 25'$, $n_{D30°}$ 1,55611, acid v. 0,6, ester v. 289,8. It was not completely soluble in 10 vols. of 70 p. c. alcohol, but with its own vol. of 80 p. c. alcohol a. m. it made a clear solution. At a warm temperature the oil formed a yellow liquid, but even at room temperature it solidified for the most part. Freed by suction, the crystals, after being recrystallised from alcohol, had the m. p. of methyl cinnamate (36°). By saponifying the esters it was possible to isolate the cinnamic acid (m. p. 133°) and the methyl alcohol. The last-named was identified from its b. p. and from conversion into formaldehyde.

The oil, when separated by suction from the crystals after strong cooling, still possessed the intense odour of methyl cinnamate. Its constants were: $d_{15°}$ 1,0404, $n_{D20°}$ 1,54932.

By repeated distillation at ordinary pressure, during which it passed over between 230 and 260°, the oil was freed as far as possible from methyl cinnamate (b. p. 255 to 260°) but this could only be done imperfectly. When the first runnings had been saponified only a small quantity of oil of a faintly camphoraceous odour was left behind; but it was impossible to detect in this fraction either camphor (with semicarbazide) or borneol (with phenyl*iso*cyanate).

An oil from *Ocimum canum* produced in the island of Mayotte and described in our *Report* of April **1908** (p. 120), had very different properties. It contained practically no ester (ester v. 2,8) but a fairly large proportion of *d*-camphor, and in these respects agreed with Charabot's oil referred to above.

Oil of Ocimum gratissimum. The great differences which exist between the oils of the various *Ocimum* species are evident from the examination of the oils of *Ocimum canum* (see above) and *O. gratissimum,* L. For, whereas the first-named oil

[1]) *Bull. du Jardin Colonial* **1903**; *Berichte von Roure-Bertrand Fils* April **1903**, 33. — [2]) *Berichte von Roure-Bertrand Fils* Oktober **1913**, 19.

consists principally of methyl cinnamate, the oil of *Ocimum gratissimum* contains considerable quantities of phenols. The golden-yellow oil examined by the firm Roure-Bertrand Fils[1]) was distilled at Dabakala (Ivory Coast). Its odour was exactly like that of ajowan oil, and its constants were as follow: $d_{15°}$ 0,9105, $\alpha_D + 0° 58'$, sol. in 1,2 vols. of 80 p. c. alcohol. It contained 44 p. c. phenols. The presence of thymol was ascertained by the m. p. (49,5 to 50,5°).

The botanical examination of the raw material was caried out by E. G. Camus.

Recently we received a similar oil from Central Africa. It possessed the following characters: $d_{15°}$ 0,9055, $\alpha_D + 0° 50'$, $n_{D20°}$ 1,49373, acid v. 0,4, ester v. 3,5, not completely soluble in 10 vols. of 70 p. c. alcohol, but soluble in 9 vols. a. m. of 80 p. c. alcohol with a minimum opalescence, and also in half its own vol. a. m. of 90 p. c. alcohol. The oil had a pale-brown colour and a thyme-like aroma. It contained 35 p. c. thymol.

Olibanum Oil. See under Frankincense Oil, page 62.

Orris Oil. Our informants in Leghorn have sent us the following report which, as usual, we reproduce textually: —

> Referring to our report on Florentine orris-root of last September, we are to-day in a position to confirm the statement that the crop of the season 1913/14 has yielded a maximum of . . . . . 650 tons.
> Up to the end of February 1914, there has been shipped to Germany, France, England, and America . . . . . 550 „ .
> Leaving an available balance on March 1 of . . . . . 100 tons.
>
> Of this quantity about 70 tons are still in the hands of some of the larger producers, who command plenty of capital and have therefore been able, in anticipation of higher prices, to keep their supplies off the market. In the present season speculators have preferred to restrict their operations owing to the high prices and the loss of interest and general risk involved thereby; hence the quantity of which they still dispose is estimated at present at about 30 tons only, of which the larger part must probably be used to cover current contracts. This season, during the months of September to December, the United States have bought a great deal more Florentine orris root in Europe than they usually do, and as for the rest, the consumption in Europe has not diminished, but has rather been stationary, and the tendency of prices since the beginning of the season has steadily been upwards. The first transactions of new root this season were put through on the basis of 150.— *Lire* per 100 kilos taken at the place of production, and to-day it is impossible to buy from any of the growers at less than 170.— *Lire* per 100 kilos, at the place of production. From September 1913 up to the present time there has been no sign of any weakening of the market and the opinion is general that prices may rise still further, because consumers will still require considerable quantities before next September, when the new root comes to market. Although the above may appear to be a very optimistic view on the part of the growers, it is nevertheless probable, in the face of the prevailing scarcity of available root, that the present prices may at least be maintained without difficulty until the end of the season.
>
> As regards the new crop of Florentine orris root, it is very difficult at at present to make estimates of any accuracy. But taking into account that new plantations will be ready to produce crops next season it may be expected with some confidence that, barring disease or other unforeseen happenings, the coming crop will give a larger outturn than did the last.

Pagsainguin Oil. In our *Report* of October 1907, p. 40, we described a sample of oil which had been sent to us at the time by the Bureau of Science at Manila

[1]) *Berichte von Roure-Bertrand Fils* October 1913, 21.

under the name of "Pagsainguin Oil", and which was said to be the product of the resin of *Canarium Cumingii*, Engl. (N. O. *Burseraceæ*). It was pointed out afterwards that the oil, as appeared from a paper by R. F. Bacon[1]) was derived from another species of *Canarium*, to wit, *C. villosum*, F. Vill. Bacon found an oil of this kind to contain *d*-α-pinene, dipentene, and formic acid. We suspected at the time that the principal constituent of our sample, a pale-green oil ($d_{15°}$ 0,8627; α_D +11° 3′; $n_{D20°}$ 1,47245; sol. in 3 vols. a. m. of 90 p. c. alcohol), was *p*-cymene. We are now able to report with regard to the chemical constitution of this oil that our surmise has been confirmed, but that for the rest we have found it to contain other hydrocarbons than those which had been found in it by Bacon.

The sample at our disposal amounted only to about 45 grams; it distilled over between 34 and 50° (4/5 mm.) and was split up in the following fractions: —

1. 34° (4 to 5 mm.); abt. 20 gr., camphoraceous odour.
2. 34 to 43° (4 to 5 mm.); abt. 5 gr., p. b. 167 to 171° (ord. press.).
3. 43 to 50° (4 to 5 mm.); abt. 15 gr., odour of cymene.
4. Residue: resinified oil.

The portions of the first fraction which distilled over between 161 and 164°, representing about 8 grams, were hydrated by the familiar method with glacial acetic and sulphuric acids; the ester-fraction (b. p. 65 to 80° at 5 mm.) of the reaction-product being saponified with alcoholic potash. Although the saponified oil had a pronounced odour of *iso*borneol, we were unable to obtain from it any solid alcohol by cooling. Lack of material precluded us from definitely establishing the presence in the fraction of camphene.

Portions of the 1st and 2nd fractions boiling between 164 and 169° (7 grams) were oxidised with an alkaline permanganate solution under ice-cooling, for the purpose of testing them for β-pinene. The salt which crystallised out from the condensed oxidation-liquid in the form of the characteristic scales of sodium nopinate, afforded nopinic acid when acidulated, and after repeated recrystallisation this acid melted from benzene at 124 to 125°. The presence of β-pinene was thereby established.

The characters of the 3rd fraction were as follows: $d_{15°}$ 0,8620, α_D + 8° 26′. It gave no phellandrene-reaction. The bulk distilled over between 174,5 and 176°; in view of its unmistakable odour of *p*-cymene it was first of all oxidised with dilute permanganate solution, after which the unattacked oil, driven off with steam (which possessed almost the same properties as those of the original fraction), was further oxidised with strong permanganate solution at water-bath temperature. We only succeeded in obtaining minute quantities of *p*-hydroxy*iso*propylbenzoic acid, m. p. 155°, from which, by heating with hydrochloric acid, *p-iso*propenylbenzoic acid, m. p. 159 to 160°, was obtained, proof of the presence of *p*-cymene being thus afforded. It is certain, however, that the oxidised oil contained, in addition to a considerable proportion of *p*-cymene, another hydrocarbon of the terpene series. The portions of fraction 3 which boiled between 176 and 179° were tested for terpinene (nitrosite reaction) with a negative result.

According to the investigation described above, pagsainguin oil therefore contains besides *l*-β-pinene, *p*-cymene, and probably also camphene. In any case, β-pinene forms the principal constituent.

[1]) *Philippine Journ. of Sc.* **5** (1910), A, 257; *Report* April **1911**, 60.

Palmarosa Oil. As has been already stated by us, high prices were asked and paid for the new distillate, although, generally speaking, the declining tendency in the value of all geranium oils greatly diminished the desire to buy. But as next to no stocks were held in Europe there was nothing for it but to pay the prices asked, in order to make it possible to satisfy the requirements of regular buyers. The Indian dealers have been clever enough to come into the market with offers only at intervals, and for the present therefore, slight fluctuations apart, the high prices could be maintained. It is impossible to say with any degree of certainty whether this will also be the case in the future, because the course of prices is influenced by too many factors which cannot be foreseen from our point of view. Our popular Palmarosa Oil Substitute has continued to meet with undivided approval, and at times we even found it impossible to execute all orders with that promptness to which our clients are accustomed from us. The supplies of raw material came in rather irregularly and we must therefore still plead for some consideration. Everything considered, we doubt very much whether we shall be in a position to continue to sell at the present prices, which leave no margin whatever for reduction.

Parsley Oil. We have at length succeeded in acquiring advantageously some parcels of distilling-material of good quality, partly from Hungary and partly from the Hartz district, and we have thus been enabled to effect a commensurate reduction in prices. French seed has played no part, because the price asked for it was too high. We have fortunately also succeeded once more in finding a parcel of parsley seed containing apiol, and we are therefore at last able again to offer a little pure apiol. This article, which is official in France, has been unobtainable for years.

Patchouly Oil. Although the oil-yield of the raw material was often poor, we have been again in a position to reduce the quotations somewhat, and by doing so we have secured a good deal of business. The fact that very large parcels have passed into the hands of middlemen is a proof that the present quotations are worthy of attention, for the middlemen no doubt calculate that sooner or later the market will assume a more favourable aspect than it has worn during the last few months. Our stocks are always considerable, and we are therefore able to supply our friends with an oil which has been properly matured.

M. Lehmann[1]) has observed that samples of patchouly oil distilled from Penang leaves of last year's crop were abnormal, insofar as their specific gravity was too low, their rotation too slight and their solubility insufficient as compared with normal samples. The density fell as low as 0,95 and the rotation to $-42°$; in the case of two samples of these oils, which were distinguished by a particularly exquisite and intense aroma, the values were even lower than this: d 0,935 and 0,937, α_D — 9 and $-34°$. In many cases about 6 vols. of 90 p. c. alcohol were needed to make a clear solution. The yield also left to be desired, being in certain instances not above 2 p. c.

Without entering into particulars, mention may here be made of an article by E. M. Holmes[2]) in which, illustrated by numerous figures, the parent plants of the patchouly-herbs of commerce are described, and a synopsis is given of his earlier publications on the subject[3]).

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[1]) *Chem. Ztg.* **37** (1913), 1589. — [2]) *Perfum. Record* **4** (1913), 369, 418. — [3]) Comp. *Report* April **1906**, 49; April **1908**, 79; November **1908**, 95; October **1909**, 92.

Pennyroyal Oil. The sale of this oil has left a good deal to be desired, and in spite of the scarcity of oil from the Spanish producing districts, it has therefore not been necessary to increase the price. It would appear moreover that its use in the soap-industry has declined. American pennyroyal oil is also unchanged.

A case of poisoning by a single dose of 7 grams pennyroyal oil is described in an English periodical [1]). Half an hour after taking the dose the patient became distracted, and finally she had an attack of frenzy which lasted four hours. An emetic was then administered, after which she recovered fairly rapidly. On the next day she was quite well again.

Peppermint Oil, American. As is always the case at the present season, it is impossible to say much that is of value about the prospective development of the peppermint oil cultivations in Michigan and Indiana. Our New York friends report that it is as yet too early to discover what damage has been done to the roots by the winter. In amplification of our report of last October they observe: At the beginning of last August, owing to the poor appearance of the fields, we estimated the result of the crop at 225000 lbs., but since then it has turned out that the total production was close upon 265000 lbs. of oil. Fine rainfalls in August assisted, at any rate to some small degree, the development of the plants, and although it was too late to improve the growth of the leaves to any appreciable degree, yet the oil-content was increased, and this accounts for the surplus production. In the months of September and October the turnover was fairly brisk, but in November and December the market calmed down again, consumers at this period maintaining an attitude of great reserve. One of the largest growers in the West then brought his oil to market and prices fell by as much as 10 to 15 cents per lb. Now, however, the growers have cleared off their stocks of oil, which have passed into the middlemen's hands, so that the situation has again grown firmer, and it is to be expected that during the summer everything possible will be done to drive up the prices once more. With the new crop, but not until then, the position may possibly undergo a change. Thanks to our timely purchases at advantageous prices we have been in a position to supply the friends of our two popular brands "F S & Co." and "F B" at cheap rates, and it is only the recent cable advices of serious upward movement, said to be due to bad weather in the West, that have induced us to follow the market, at any rate to some extent.

We have recently noticed that the shipments of peppermint oil which have reached us from America contained an exceptionally large percentage of menthone. Upon enquiring from our New York branch house as to the probable cause of this phenomenon, our American friends consulted their scientific adviser, Dr. C. Kleber, of Passaic, N. J., who has sent us the following statement on the subject: —

The American peppermint oil samples of last year's crop showed certain peculiarities in respect of their characters, as will be observed from the subjoined table, in which the oils are recorded in the order in which they arrived at New York. As, owing to the urgency of the demand, the oils were delivered fresh from the still, it is probable that the sequence in the table corresponds closely with that in which the parcels were produced.

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[1]) *Pharmaceutical Journ.* **92** (1914), 10.

No.	Received	$d_{25°}$	α_D	Total menthol	Menthone
I.	21. August	0,8995	— 25° 27′	49,7 %	18,8 %
II.	3. September	0,8983	— 24° 20′	48,4 %	16,8 %
III.	10. „	0,900	— 24° 14′	51,7 %	17,98 %
IV.	10. „	0,904	— 24° 28′	50,2 %	16,98 %
V.	10. „	0,902	— 24° 30′	50,2 %	17,7 %
VI.	10. October	0,905	— 23° 18′	53,5 %	14,0 %
VII.	10. „	0,901	— 26° 12′	56,1 %	13,9 %
VIII.	11. „	0,902	— 25° 30′	55,8 %	16,7 %
IX.	20. „	0,903	— 23° 49′	56,4 %	15,2 %

The rotation is normal, and the specific gravity differs from the normal at most to the extent that the parcels which came to hand first were a little lighter than usual, but the menthol-content of these first arrivals is comparatively low, falling even below the Pharmacopœia-limit of 50 p.c. On the other hand, the menthone-content in these cases considerably exceeds the normal value. In the later deliveries, those of October, the oils are again quite normal, except from a slightly increased menthone content. In all probability these peculiarities are due to the abnormal conditions which prevailed during harvesting, as already depicted in our last *Report,* which compelled the producers to distil the herb before it had reached full maturity. From the figures it may be inferred that in the earlier stages of growth considerable proportions of menthone are formed in the plants, and that this is partly converted into menthol during the later stages of development.

Peppermint Oil, Chinese. Some time ago the Imperial Institute in London[1]) received a sample of peppermint oil from Hong Kong. As the oil was of a deep-red colour, it was purified by steam-distillation, after which it was found to possess the following constants: $d_{15°}^{15°}$ 0,918, α_D — 44° 40′, sol. in 2,5 vols. of 70 p.c. alcohol. It contained 50,69 p.c. of free and 13,55 p.c. of esterified menthol.

The peppermint oil which is distilled in the neighbourhood of Hong Kong[2]) for purposes of export or for sale to the Chinese, is almost colourless; it has an agreeable odour of peppermint, and resembles the oil containing menthol[3]) which is exported on a large scale, chiefly from Japan, to Europe and the United States. In many respects the Chinese oil is said to be superior to the Japanese article. The oil as prepared by the Chinese realizes in the local markets prices varying from $ 130.— to $ 230.—, currency, per picul (133⅓ lbs.) = $ 0.47 to $ 1.08 gold per lb. Peppermint crystals are are also exported in large quantities; the present value is about $ 2200.— local currency per picul, = $ 7.75 gold per lb.

Peppermint Oil, English. Our forecast of the probable course of the English market has proved to be correct. No changes of any importance have occurred, and in spite of the declining interest shown in Mitcham peppermint oil, and its supersession by rectified American oil, the leading brands were able to maintain their value. We hold sufficient stock to last us until the new crop, but we do not regard it as out of

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[1]) *Bull. Imp. Inst.* **11** (1913), 434. Comp. *Report* October **1910**, 96; April **1913**, 83. — [2]) *Daily Cons. and Trade Rep.*, Washington **17** (1914), Nr. 56, p. 906. — [3]) The original report has "mentholised". Should this not be "dementholised"?

the question that the prices may tighten in the course of the summer, when the supplies in England are nearing an end.

Peppermint Oil, Japanese. The market in this important article, of which the position notoriously directly affects the price of menthol, has been exceedingly interesting during the last few months. Influenced by the general reports of a record-crop a very animated business of new crop oil for shipment at falling prices began to develop shortly after the publication of our October *Report*. But when the slump began to progress more quickly the buyers retired from the market and a state of listlessness set in which gradually led the bear-party among the Japanese firms to make new offers of some importance at quotations which it was simply impossible to resist. The price quoted was 6/– for assorted shipment, which works out at about 9/3 for menthol and 4/– for oil. Shortly after we had succeeded in buying at least a few hundred cases for shipment during the spring at these low prices, various rumours suddenly obtained currency which resulted in a rapid rushing-up of the market. In one quarter it was asserted that the greater part of the 1913 output had been taken out of the market by a combine of several Japanese refiners, in order to obviate a further slump in prices, while other reports said that the farmers, alarmed at the low prices, had petitioned the Japanese Government to establish a Monopoly for the production of peppermint, on the lines of that which is already in successful operation for camphor. Fortunately the bull-party were not successful in giving the European and American markets an attack of nerves. Only a quite unimportant business was done at the increased quotations, and the feeling soon became calm again. The tendency of prices turned in a different direction, but without, for the present, reducing the market again to the low level which prevailed at the beginning of the year. This is probably connected with the fact the bear-sellers have been compelled to cover themselves against their January/March sales, and that as a consequence no considerable supplies could accumulate at the ports of shipment at the other side. It must be left to the future to show what course the Japanese menthol- and peppermint-oil market will take. We are inclined to think that the exceptionally large yield of the 1913 must depress the market, but the trade in these two important articles has so often brought surprises in the past that it is better to abstain from any forecasts about the future. In any case, the fact must be taken into consideration that reports are also in circulation which talk of a serious restriction in the extent of cultivation this year, and hold out the expectation of a considerable falling off in the output during the coming season. It will not be possible to form an even approximately reliable idea of the position on the basis of figures before the ensuing summer.

The German Consul at Kobe, Herr Ohrt, has had the courtesy to bring to our notice that the figures given under the heading "peppermint oil" on p. 81 of our *Report* of April **1913** do not refer to peppermint oil, but to fatty oils in general, a fact which is not self-evident in the original, the Financial and Economic Year Book for Japan, from which we took the data. Herr Ohrt informed us at the same time that the figures quoted for "peppermint" represent the value of the annual production of menthol and peppermint oil together. The annual exports of peppermint oil up to the year 1912 have always been below 700 000 yen. We now recapitulate the figures under their proper denominations up to, and inclusive of, the year 1912[1]).

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[1]) *Finanz. u. wirtsch. Jahrbuch f. Japan* **13** (1913), 72, 102.

	Production of peppermint oil and menthol	Menthol-Exports		Production of peppermint oil and menthol	Menthol-Exports
1899	— Yen	195 424 Yen	1906	2 305 076 Yen	517 215 Yen
1900	— „	172 501 „	1907	1 322 772 „	337 865 „
1901	— „	437 051 „	1908	633 998 „	263 937 „
1902	772 104 „	463 719 „	1909	1 340 480 „	490 525 „
1903	1 119 403 „	804 401 „	1910	1 679 851 „	648 857 „
1904	2 308 269 „	1 090 542 „	1911	2 870 882 „	963 220 „
1905	2 183 231 „	797 624 „	1912	— „	1 589 729 „

A report from the same Consul, dated 26th November 1913[1]), gives the following particulars:—

The production of peppermint oil[2]) in Japan is subject to great fluctuations. This is partly a result of climatic conditions, the peppermint-plant being extraordinarily sensitive, and partly it is due to the fact that planting follows the prices. High prices are followed by an increase in the area under cultivation in the following year, and *vice versâ*. As high prices ruled in the year 1911, both cultivation and production in the year 1912 increased to an extraordinary extent.

No statistical details of the 1912 crop are yet available, but the output is estimated at about double that of a normal one.

In the past only three Japanese firms, namely Kobayashi, Suzuki, and Yazawa have been regarded as buyers-up in the market, but in the year 1912 a fourth firm made its appearance in this capacity, this being the English house of Samuel, Samuel & Co., who bought up about one-third of the entire Hokkaido-crop. In doing this the firm received the support of the Japanese local authorities, whose object it was to break the ring of the three old buying-firms.

As a result of this competition the buying-up prices reached an exceptionally high level, notwithstanding the increased quantity offered. Towards the turn of the year 1912 crude peppermint oil from the Southern districts realized from 9,50 to 10 yen per kin, and Hokkaido peppermint oil fetched 7,50 yen. Menthol crystals realized up to 18 and even 20 yen per kin; they sold in the London market at 42/- per lb.

These high prices had again the effect of greatly increasing the cultivation in Japan; the output of the 1913-crop being estimated at about 450 000 kin of crude peppermint oil in Hokkaido, and 400 000 kin in the Southern Districts, which together is from 3 to 4 times as much as the figures given for the year 1911 (264 000 kin). Added to this is the fact that the said firm of Samuel, Samuel & Co., having been unable to introduce its brand, up to then unknown in Europe, quickly enough, was left with a considerable part of its stock, and carried over considerable quantities of the 1912-crop into the present season, finding itself compelled to sell these at considerably reduced prices.

As a result of this concatenation of circumstances, the peppermint-market suffered such a slump during the last few months, as is unusual even in this speculative article. At the present time (end of November) the following prices per kin are quoted for shipment in the first quarter of 1914; crude oil (Hokkaido) 3,20 yen; ditto (Okayama) 4,20 yen; menthol crystals 6 yen and dementholised oil from 2,70 to 2,80 yen. These prices are only about one-third of those which were paid a year ago.

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[1]) *Nachrichten f. Hand., Ind. u. Landw.* **1914**, No. 1. — [2]) The original report has "peppermint". As, generally speaking, this term is held to the plant, we have here altered the expression to "peppermint oil".

It is further to be noted that the cultivation of the peppermint-plant is still remunerative at prices of 2,50 yen in Okayama, &c. This is due to the fact that in the North only corn and bean-fruits can be grown as substitutes of peppermint, and that these crops, owing to the undeveloped condition of the means of communication, entail great expenses for transport upon the farmers, whereas the product of the peppermint is collected from them free of charge by the agents. In the South, on the other hand, when peppermint ceases to be remunerative, the farmers turn to rice, which pays better.

With regard to the future course of the peppermint market only this can be said, that the cultivation in Japan in the year 1914 will unquestionably decline very considerably. But it is doubted whether this will result in an early advance in prices. Peppermint oil and menthol can be kept for years, and it is therefore to be assumed that the industries in which these articles are used will cover their requirements at the present low prices for a long time ahead.

According to a statement in the *Japan Chronicle* of 14th November 1913, Chinese peppermint oil (see p. 77) has also appeared upon the market lately, but it is thought that at the present prices this product may not be able to compete with the Japanese oil.

In our last October *Report* (p. 87) we referred to an article by Thoms, which had appeared in the *Apotheker Zeitung*, concerning several samples of oil distilled from Japanese peppermint which had partly been grown in Germany and partly in German South-West Africa. The results of this research have now also been published in the *Arbeiten aus dem Pharmazeutischen Institut der Universität Berlin* (pp. 77, Urban & Schwarzenberg, Berlin and Vienna) of which Thoms is the Editor. Special mention should be made of the excellent illustration of *Mentha canadensis* var. *piperascens*, Briquet, the parent plant of Japanese peppermint, which is given in the article.

Peru Balsam Oil. As long ago as the year 1899, H. Thoms[1]) isolated from Peru balsam oil an alcohol, peruviol, to which he assigned the formula $C_{13}H_{22}O$. As this body was reputed to possess valuable aromatic properties, and as since then nothing has been published about it, we have now prepared and investigated the substance, with the object of testing its practical usefulness. The results of our investigations are described below: —

The sample of Peru balsam oil under examination possessed the following constants: $d_{15°}$ 1,1200, $\alpha_D + 0° 55'$, $n_{D20°}$ 1,57177, acid v. 36,4, ester v. 228,2, sol. in 0,5 vols. a. m. of 90 p.c. alcohol.

With the object of isolating the alcohol, the oil was saponified with alcoholic potash; the alcoholic portions were driven over by steam after the spirit had been distilled off. The first body to pass over was a large quantity of benzyl alcohol, which sank in water, and towards the end of the manipulation there passed over a light oil with a characteristic balsamic odour. This body, after being purified by repeated fractionation, was found to possess the following characters: b. p. 125 to 127° (4 mm.), $d_{15°}$ 0,8987, $\alpha_D + 12° 22'$, $n_{D20°}$ 1,48982.

A previously prepared product from Peru balsam oil had exactly similar properties. As the examination of the body in question showed it to be identical with a sesquiterpene alcohol, possessing the structure $C_{15}H_{26}O$ (Hesse and Zeitschel's nerolidol)[2]), whereas on the other hand its physical and chemical properties also

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[1]) *Arch. der Pharm.* **237** (1899), 274; *Report* October **1899**, 49. — [2]) *Journ. f. prakt. Chem.* II. **66** (1902), 481; *Report* April **1903**, 53.

revealed a considerable similarity with those of peruviol, we set forth below a comparative table of the constants of the two preparations: —

	Peruviol (Thoms)	previous preparation (Schimmel & Co.)	new preparation (Schimmel & Co.) [1]	Nerolidol (Hesse and Zeitschel)	Nerolidol (Schimmel & Co.)
B. p. .	139 to 140° (7 mm.)	133° (7 to 8 mm.)	125 to 127° (4 mm.)	128 to 129° (6 mm.) 276 to 277°	125 to 127° (4 to 5 mm.)
d . .	0,886 (17,5°)	0,8819 (15°)	0,8987 (15°)	0,880 (15°)	0,8801 (15°)
α_D . .	about + 13°	+ 13° 40′	+ 12° 22′	+ 13° 32′	+ 12° 48′
$n_{D20°}$.	—	—	1,48982	—	1,48023

Our nerolidol preparation was obtained by fractionating the high-boiling constituents of neroli oil, after previous saponification. The carefully-purified nerolidol, especially that portion of it which had distilled over with steam, had the characteristic, faint but pleasant, balsamic odour which appertained to our alcohol isolated from Peru balsam oil. Our surmise that both preparations represented the same sesquiterpene alcohol was found to be correct. In the course of 3 to 4 weeks, during which the substances were allowed to stand, both afforded, with phenyl*iso*cyanate, a phenylurethane which, when purified from methyl alcohol, melted between 37 and 38°. A mixture of the two derivatives suffered no depression of m. p. After prolonged treatment with alcoholic potash at a water-bath temperature the alcohol with its characteristic smell was again eliminated from it. The combustion-values of the phenyl*iso*cyanate point to a sesquiterpene of the formula $C_{15}H_{26}O$: —

0,1522 gr. subst.: 0,4306 gr. CO_2, 0,1288 gr. H_2O,
0,1773 gr. subst.: 0,5048 gr. CO_2, 0,1537 gr. H_2O.

	1.	2.		
Found C	77,15	77,65	Calc. f. $C_{22}H_{31}NO_2$	77,42 %
H	9,42	9,64		9,09 %.

Hesse and Zeitschel had already established the same formula by combustion of nerolidol. This fact should prove the identity of the two bodies.

Now, when the constants of our two preparations (from Peru balsam oil) are compared with those of Thoms' peruviol, and again with those of nerolidol, it will be seen that there is a considerable difference in specific gravity, not only between our new preparation and peruviol, but also between peruviol and nerolidol, and again between our new preparation and nerolidol. But as all these preparations are in good concordance so far as their other properties and constants are concerned, it is certainly highly probable that they represent one and the same body; contaminated in the case of our alcohol from Peru balsam oil (new preparation) by small admixtures of a heavier body. We were unable to determine what was the nature of this admixture to our preparation. Although the alcohol-fraction yielded a small amount of benzoic acid on oxidation with permanganate, there could be no question of benzylalcohol (b. p. 78° at 4 mm.), because the fractions following the nerolidol on distilling had a higher specific gravity and yielded on oxidation a larger proportion of benzoic acid than did the lower-boiling alcohol-fraction. The latter, also, was free from esters. Oxidation of the nerolidol-fraction with an insufficient quantity of permanganate merely led to an increase of specific gravity; the admixture, therefore, was less easily attacked than was nerolidol. Treatment with bisulphite liquor showed the fraction to be free from vanillin or other aldehydes.

[1] The nerolidol content of Peru balsam oil does not exceed 2,5 p. c.

The chemical behaviour of the alcohol also was the same as that of peruviol. In agreement with the observation of Thoms, we found that nerolidol can only be very incompletely esterified. We have applied to it several methods of esterification, but all with a negative result. Our preparation, like that of Thoms, absorbed 4 atoms of bromine in a glacial acetic acid solution. With formic acid the alcohol turned turbid, probably as a result of the elimination of water. With permanganate we obtained no characteristic decomposition products.

We may observe in passing that the value 214 determined by Thoms from the estimation of the molecular weight is more in concordance with a formula $C_{15}H_{26}O$ (for which theoretically 222 is required), than with a formula $C_{13}H_{22}O$, of which the theoretical value is 194.

From the above it is fair to assume that Thoms' peruviol also consisted of nerolidol, at any rate in part, but that owing to some contamination with a body of the same b. p. its composition had suffered such a change that combustion gave values agreeing with the formula $C_{13}H_{22}O$.

Petitgrain Oil. As the political disturbances in Paraguay continue, the preparation of petitgrain oil is still being carried on under difficulties, and the supplies are not flowing by any means so freely as they did some years ago, when it looked as if, owing to over-production, the article was on the way to ruin. The prices of the few brands from reliable sources of supply which are still in existence are therefore held at correspondingly high levels, and would certainly have advanced still further if during the last few months the demand had not left a great deal to be desired.

The difficulties existing in the conditions of production of American petitgrain oil have induced the manufacturers in the South of France to pay more attention to the French oil of petitgrain, the distillation of which had lost almost all its importance within the last ten years. In 1913 from 300000 to 310000 kilos of orange-shoots were worked up. They yielded about 650 kilos of oil, for which 85.— *fcs.* per kilo was asked. We do not know whether it has been found possible to sell the output at this price, which appears to us to be very high, considering that, for example, our artificial neroli oil, a product possessing all the properties and advantages of genuine neroli oil, only costs about 120.— ℳ per kilo, and that Paraguay petitgrain oil of the best quality is being offered by first-hand holders at 30.— *fcs.* We are hardly ever asked for French petitgrain oil, which in our view has become quite obsolete, and for this reason have omitted it from our price-lists.

In the course of an investigation of petitgrain oil[1]) carried out by us in the year 1902, we obtained, in addition to other terpenes, a fraction possessing the odour of pinene, from which repeated attempts failed to separate out pinene nitrosochloride. It was therefore to be assumed that this fraction contained β-pinene, the identification of which is particularly easy when recourse is had to nopinic acid, a body discovered by A. von Baeyer and Villiger[2]), and by proceeding by the method indicated by Wallach[3]).

The sample of petitgrain oil which was recently tested by us for β-pinene, possessed the following constants: $d_{15°}$ 0,8886, α_D + 1° 3′, ester v. 120, corresponding to 42 p. c. ester. By repeated fractionation of the terpenes, a portion with a b. p. between 167 and 170° ($d_{15°}$ 0,8474; α_D — 7° 10′) was separated. When oxidised with potassium perman-

[1]) *Journ. f. prakt. Chem.* II. **67** (1903), 321; *Report* October **1902**, 68. — [2]) *Berl. Berichte* **29** (1896), 22. — [3]) *Liebigs Annalen* **356** (1907), 228; *Report* April **1908**, 59.

ganate in an alkaline solution, this fraction afforded a liberal yield of the sodium salt of nopinic acid, a body which crystallises in brilliant leaflets, from which, by resolving it with sulphuric acid, we obtained nopinic acid, m. p. 126 to 127°. For purposes of further identification we prepared from the nopinic acid nopinone, which, with benzaldehyde, condensed readily into the benzylidene compound $C_9H_{12}O:CHC_6H_5$[1]), m. p. 107°.

The surmise that petitgrain oil belongs to the class of oils containing *l*-β-pinene, was therefore confirmed.

A sample of petitgrain oil distilled in Jamaica has been examined at the Imperial Institute in London[2]). The oil possessed the following constants: $d_{15°}$ 0,8884, α_D — 6° 45′, sol. in its own vol. a. m. of 80 p.c. alcohol. It contained 31,6 p.c. free and 55,65 p.c. esterified alcohols.

The oil is noteworthy for its comparatively high degree of lævo-rotation, for in the case of the commercial oil, which comes mostly from Paraguay, the rotation varies from + 5° to — 2° 43′. It is possible that this may be due to the circumstance that the crude material consisted principally of leaves, at any rate experiments made many years ago by Charabot and Pillet[3]) showed that the leaves of the bitter orange tree yielded oils which were more lævorotatory than the other oils. Incidentally we may here refer to another oil from Jamaica which was forwarded to us a long time ago. Its characters were similar to those of the oil above referred to, but it contained rather less ester: $d_{15°}$ 0,8846, α_D — 6° 30′, acid v. 0, ester v. 82,0 = 28,7 p. c. ester calc. as linalyl acetate, sol. in 2 vols. a. m. of 70 p. c. alcohol.

Pimento Leaf Oil. The Imperial Institute in London[4]) reports on a pimento leaf oil distilled in Jamaica (from *Pimenta officinalis*, Lindl., N. O. *Myrtaceæ*) which possessed the following properties: $d_{15°}$ 1,026, α_D — 5° 30′, sol. in 1,6 vols. of 70 p. c. alcohol. 68,6 p. c. of the oil consists of phenols, principally eugenol.

Pine-needle Oils. Nothing new is to be reported on the present occasion concerning Siberian pine-needle oil, a perfumery-material which is highly valued in the manufacture of all technical products, pine-needle oil from *Abies pectinata*, which is used in the numerous preparations for purifying the air and for spraying, or oil of *Pinus Pumilio*. Oil from the cones of *Abies pectinata (ol. templinum)* was somewhat scarce, but here also the supplies from Switzerland were sufficient, and there has been no necessity to advance the quotations.

C. Th. Mörner[5]) has tested a series of oils from the needles of conifers and has ascertained that a considerable amount of sophistication is practised with these oils, and that great caution is therefore advisable in buying. Of 28 samples of commercial oils, Mörner states only 15 could be described as of good quality. Turpentine oil is very commonly used as an adulterant. Such adulteration cannot be detected by isolating the pinene, because pinene is a normal constituent of all the oils from conifer-needles; only serious additions of turpentine oil are detectable, owing to the fact that the oil-fraction with b. p. below 165° is larger in proportion than is the case with pure oils.

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[1]) Wallach, *Liebigs Annalen* **313** (1900), 365; *Report* April **1901**, 61. — [2]) *Bull. Imp. Inst.* **11** (1913), 437. — [3]) *Bull. Soc. chim.* III, **21** (1899), 73. — [4]) *Bull. Imp. Inst.* **11** (1913), 438. — [5]) *Svensk Farmaceutisk Tidskrift* **1913**, No. 18, 19; *Apotheker Ztg.* **28** (1913), 766.

H. Helch[1]) has now tried to discover whether it would not be possible to trace the addition of turpentine oil by estimating the bromine value. He estimated this value by the method worked out by Mossler[2]). The results obtained were not very satisfactory, because pure conifer-needle oils are found in commerce with bromine values corresponding to those of certain turpentine oils. The values ascertained by the author included the following: oil of *Pinus Pumilio* from 212 to 243, a sample of pine-needle oil 255, three samples of Siberian pine-needle oil from 110 to 122, turpentine oils from 227 to 268[3]). In the fraction with b. p. below 165°, which contains the pinene, the bromine value was invariably higher, and in that with b. p. above 165° it was invariably lower, than in the original sample. From these results, Helch has acquired the conviction that for the oils of the conifers the estimation of the bromine value is but a very imperfect addition to the existing methods of testing and that, taken by itself, it affords no criterion to the purity of such oils.

We further find in Helch's lecture the statement that in the case of pure oils of conifer there was but little difference between the optical rotation of the original sample and that of the fraction with b. p. below 165°. All the samples of oil of *Pinus Pumilio* examined by him contained fractions boiling below 165°, but as a rule such fractions did not exceed 10 p.c. by volume of the sample.

We have recently received a claim relating to oil of *Pinus Pumilio* which appears to us to be rather comical, inasmuch as it showed that the person who bought the article had no idea what the smell of a really pure oil distilled from *Pinus Pumilio* was like. The details of the incident are as follows: We had supplied oil of *Pinus Pumilio* to a pharmacist, who in turn had sold it to a hospital. By the last-named the oil was rejected, on the ground that owing to its bad smell it was quite unfit for clinical purposes, and it was suggested that there had been some mistake. As a matter of fact there was no fault to find with the smell of the oil, which had the typical aroma of a good oil distilled in Tyrol, and we therefore procured from our pharmacist-client a sample of the pine-oil which had been previously used and approved by the Doctor in charge of the clinic. We examined the sample, and found that this oil (which, by the way, had been supplied by a Hamburg firm), was adulterated, and that consequently, its aroma differed from that of pure oil of *Pinus Pumilio*. Its characters were as follows: $d_{15°}$ 0,8868, α_D — 12° 24′, acid v. 0,9, ester v. 35,3 = 12,4 p.c. esters (as bornyl acetate), soluble in 7 vols. a. m. of 90 p.c. alcohol with opalescence. That the oil was adulterated is clear from the mere fact that both the sp. gr. and the ester-content are much too high. Apparently it had been doctored with Siberian pine-needle oil; at any rate such an addition would make a mixture with the constants enumerated above.

The case quoted shows clearly the conditions which prevail in the pine-needle oil trade, and indicate how imperfectly the consumer is sometimes able to judge the quality of these oils. It is to be regretted when this ignorance goes as far as it did in the present case. To be sure, one cannot reproach a person because he does not like the aroma of oil of *Pinus Pumilio*, for that is a matter of taste, and there may be many who for certain purposes would give the preference to oil from the cones

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[1]) *On the Examination of Pine Needle Oils.* A lecture given before the 8th Section (Pharmacy, Pharmacognosy and Pharm. Chemistry) of the 85th Congress of German Naturalists and Physicians at Vienna. From a reprint from the *Pharm. Post.* **1913**, kindly sent to us. Also comp. *Chem. Ztg.* **37** (1913), 1176. — *Apotheker Ztg.* **28** (1913), 806. — *Zeitschr. f. angew. Chem.* **26**, I (1913), 579. — [2]) Comp. *Report* October **1907**, 116. — [3]) Wolff found for pure oil of turpentine 215 to 230, Vaubel 220 to 240. Comp. *Report* October **1913**, 101.

or needles of *Abies pectinata* or even, as in the case under review, to a mixture. But when a person expressly demands a definitely specified oil and receives the same of unimpeachable quality, it is somewhat humorous to find him reject it as inferior. Where such a state of things prevails it is no wonder that traders of a certain class exploit the conditions to the utmost of their power.

Some years ago we mentioned a paper by J. W. Brandel and M. Sweet[1]) on Douglas fir needle oil. We are now again in a position to report on this oil, A. W. Schorger[2]) having found oil of the needles of the Douglas fir (yield about 0,163 p. c.) to contain the following constituents: 25 p. c. *l*-α-pinene (nitrolpiperidide), 48 p. c. *l*-β-pinene (nopinic acid), 6 p. c. *i*- or *l*-limonene (hydrochloride; tetrabromide), traces of furfurol (colour-reaction with aniline hydrochloride), 6,5 p. c. borneol (oxidation into camphor), 6,1 p. c. esters, calculated as bornyl acetate (the acetic acid was identified from the analysis of its silver salt) and 3 p. c. of a green-coloured fraction, b. p. 125 to 205° (20 mm.) apparently containing sesquiterpene. No camphene was present in the oil, whereas Brandel and Sweet had been able to detect this terpene in the product examined by them. The constants of the two distillates also show somewhat considerable points of difference. Schorger found his oil to possess the following characters: $d_{15°}$ 0,8727 to 0,8759, $\alpha_{D20°}$ — 17,02 to — 22,17°, $n_{D15°}$ 1,4758 to 1,4780, acid v. 0,65 to 1,1; ester v. 11,13 to 24,25, ester v. after acet. 27,5 to 51,78. Brandel and Sweet record the following properties: $d_{23°}$ 0,8680, α_D — 62,5°, acid v. 0, sap. 86,6. These differences may perhaps be explained by the fact that the distillate described by Brandel and Sweet had been prepared in the State of Washington, and the oil examined by Schorger in California.

Rasamala Oil[3]). From the resin of *Canarium microcarpum*, Willd. (N. O. *Burseraceæ*), which had been received from the Moluccas, 80,4 p. c. of oil has been distilled at Buitenzorg[4]): $d_{27°}$ 0,930, α_D + 0° 28′. Sap. v. 2,8. The bulk of the oil boiled between 250 and 285°.

Rose Oil, Anatolian. With reference to Anatolian rose oil, it is reported that pretty considerable quantities of rose oil are manufactured in the neighbourhood of Isbarta (Sparta, Asia Minor), the quantity produced in the year 1912 having been 300, and in 1913 as much as 400 kilos[5]). Formerly all this oil was sold to Bulgaria, and exported thence as Bulgarian rose oil. Last year, however, the oil was bought up by a firm in Smyrna and shipped direct to Europe. It is said that the farmers of Isbarta are still ignorant of the methods of adulterating the oil, and that therefore the oil supplied by them is quite pure. The characters of the oil are as follows: $d_{15°}^{30°}$ 0,850, α_D — 3° 30′, $n_{D25°}$ 1,4605, m. p. 24 to 25°.

Rose Oil, Bulgarian. The firmness in the position of the market to which we referred in our last *Report* has been, generally speaking, maintained throughout the winter, but of course only for quality which was beyond reproach, for so-called "pure qualities" were, as always, plentifully offered on the market, and could be had at all sorts of prices. In November sales were made at about 3700.— *frs.*, a price which places the cheap quotations of the middlemen in their proper light. Naturally, at this

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[1]) *Pharm. Review* **26** (1908), 326; *Report* April **1909**, 43. — [2]) *Journ. Americ. chem. Soc.* **35** (1913), 1895. — [3]) On p. 107 of our *Report* of April **1912** we erroneously described the oil as „Rasama" oil. — [4]) *Jaarb. dep. Landb. in Ned.-Indië*, Batavia, **1912**, 57. — [5]) *Perfum. Record* **4** (1913), 338. Comp. *Report* April **1902**, 60, April **1905**, 68 and October **1912**, 97.

fancy-price the turnover was only a modest one, but the fact remains that this figure was repeatedly paid. As the winter advanced the market became decidedly flatter, for it is easily understood that there was little eagerness to continue to pay such a price, particularly so because the weather was normal, and the first condition for a favourable development of the plantations during 1914 was therefore in existence. At the end of February it was reported from the neighbourhood of Kazanlik that the weather was warm, and very favourable to growth of the young shoots of the rose-trees. Of course, this report brought about a further weakening of the market. Account has still to be taken of the possibility of frosts within the next few weeks, which may destroy the at present favourable prospects, for the young shoots are very sensitive. The weather of the coming four or six weeks, therefore, will be the determining factor for the crop. It has further been found that there is no truth in the statements of neglect of the plantations during the war; hence, barring unforeseen climatic troubles, the present year's gathering may be expected to yield a good result. It is, in fact, high time for a return of favourable conditions of price in the rose oil business, for the unwillingness of consumers to continue to pay the current prices has lately become much more marked still, and we have been repeatedly told already that customers will not readily abandon the employment of artificial rose oil now that, in the meanwhile, they have grown used to it. The existing conditions of the money-market in Bulgaria should assist in keeping the demands within certain bounds this year.

In our April *Report* of 1913 (p. 88) we referred to a rose oil which had been adulterated with phthalic ester. C. Kleber[1]) reports on an oil similarly adulterated. In his case the specific gravity was extraordinarily high (1,061), and even when the sample was placed in ice-water no solid portion was separated out. The saponification value, which normally does not exceed 17, was here 295. From the saponification liquor considerable quantities of a salt crystallised out of which the acid constituents were identified as phthalic acid. Kleber concludes from the saponification value that the addition amounted to about 58 p. c.

A Bulgarian chemist, C. Taramoff[2]), who has been examining samples of otto of rose, sold on the Bulgarian market, brings to our notice quite an extensive collection of adulterated rose oils. Twenty eight samples tested by him were all more or less adulterated; he even mentions one instance of a mixture which contained no rose oil at all. Among the adulterants, palmarosa oil and alcohol occupy the principal places; among others being geranium oil, gurjun balsam oil, and artificial stearoptene. Taramoff has set out the results of his investigations in table-form, and in another table he passes in review the physical constants of 30 different samples of oils and of the different adulterants used by the producers of rose oil. Here again, palmarosa oil plays the leading part.

On the citronellol-content of rose oil, see p. 121 of the present *Report*.

Rose Oil, Persian. The British Consul at Bushire, in his report on the Persian fiscal year 1912/12[3]) refers to the production of rose oil. The output in Persia, he says, is limited to some 2500 miskals of 320 ounces annually and has hitherto only

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[1]) *Americ. Perfumer* 8 (1913), 171. — [2]) *Perfum. Record* 4 (1913), 416. — [3]) *Dipl. and Cons. Rep.*, London No. 5255 (1914), p. 37.

been used in the country itself and in India, but owing to the favourable market conditions of last year, small experimental consignments were sent to London. The price of the Persian oil ranges from 12 to 15 krans (4 s. 4 d. to 5 s. 6 d.) per small bottle, of one-eighth ounce. Adulteration is said to be practised to some extent by the distillers with both vegetable and highly-refined mineral oils. Persian attar is said to have marked qualities of its own, which makes it quite different from the Bulgarian product. One analysis made in London gave the following characters: m. p. 26 to 27°; opt. rot. 3° (— ?) refractive index 1,456.

The preparation of rose water in the district of Fars, between Bushire and Shiraz, is of greater importance. Roses have been cultivated there on a large scale for many centuries. The working-up of the rose petals, and the manufacture of the glass carboys in which the rose-water is packed, are special industries in the district.

The total output of rose water has been estimated at 400 tons, or 10000 cases yearly, and there is considerable consumption in Persia itself. The quantities exported in 1912/13 were 6,519 cases, weighing 187 tons, and 6,040 carboys weighing 82 tons to India and Bahrein. So far there has been no demand from Europe. The yield of roses was larger than usual in 1913, but owing to lack of rain a vegetable product, which is used with certain local earths in manufacturing the crude green glass carboys, was not obtainable in sufficient quantities, and there was a smaller output of rose water than usual.

Prices were in 1912/13 20 to 22 krans (7 s. 3 d. to 8 s.) per carboy containing about 39 lbs. weight, and 36 to 40 krans (13 s. to 14 s. 6 d.) per case weighing about 62 lbs. (21 bottles), or $1^3/_4$ krans per bottle.

Rosemary Oil. Throughout the time covered by our *Report* there has been no lack of oils possessing the properties of pure French distillate, nor of Dalmatian oil. The prices have undergone no change, but they will doubtless be able to maintain their present level.

Sage Oil. This article is now manufactured in Dalmatia so cheaply and is so well worth the money asked for it, that distillation here has become unprofitable. We would take this opportunity, however, of warning the producers against taking too sanguine a view of the possibilities of the demand, and of advising them to beware of over-production, in order that the satisfaction they derive from this still somewhat novel source of revenue may not be thoroughly spoilt by its becoming unprofitable.

Oil of Salvia cypria. *Salvia cypria,* Ung. et Kotschy (N. O. *Labiatæ*), a native of the Island of Cyprus, affords a pale-yellow oil[1]) with an odour reminding of camphor and of camphor oil. Two samples were found to possess the following constants: $d^{15°}_{15°}$ 0,9263 and 0,925, α_{D200} — 6° 31′ and — 22° 23′, sap. v. 13,9 and 8, sap. v. after acet. 38,9 and 36, sol. in 0,8 and in 1 vol. of 80 p. c. alcohol. This oil differs from ordinary sage oil in being lævorotatory. It contains about 75 p. c. cineol (resorcinol method) and a little camphor.

One of the above oils agrees fairly well with a sample which we received from the Imperial Institute some years ago, and which we described in our *Report* of October **1910**, p. 112. Lævorotatory sage oils of different origin are also mentioned in our *Reports* of October **1905**, 62; October **1907**, 81 and April **1909**, 82.

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[1]) *Bull. Imp. Inst.* **11** (1913), 429.

Sandalwood Oil, East Indian. Although a few large transactions have taken place from time to time, and interrupted the general quietness of this important article, the market has on the whole continued to wear that aspect of want of animation on which we commented already in our *Report* of last autumn. Even the high average prices which were realized at the 1913 sandalwood auctions in Mysore were unable to infuse life into the business, and the attempts which were made in several quarters to advance the selling prices of oil were soon recognized as failures. Only quite recently have the cheap second-hand offers disappeared, for under the pressure caused by the financial stringency in the months of October and November, most of the second-hand holders have cleared their speculative stocks. But these supplies have not yet been used up by the consumers, and so they continue to depress the market. It is probable that the prices of sandalwood oil will remain unaltered for some time to come; but how the future will shape can of course not be said with any approximation to exactitude. It is a fact that a few parcels of the wood which was bought in by the Mysore Government at the last auctions are still unsold, and it may be difficult to find buyers for them without making considerable concessions in price. In spite of the large scale on which we distil this oil we have at our disposal an abundant supply of cheap wood, which will last us for a long time to come, and we would therefore be able to reap considerable benefit from an upward movement, but notwithstanding this fact we are doing all we can to reduce the demands of the shippers, or of those on whose behalf they act, to a reasonable basis, as we are convinced that it is only by such a policy that the regular sale of large quantities of oil can be promoted. We quite appreciate that with the keen competition which exists in preparations of sandalwood oil, the manufacturers of such preparations, in view of the high prices of raw material, are not in a favourable position, and it is therefore also to our own interest to assist in facilitating their business by helping to bring about lower prices for sandalwood oil. It remains to be seen, however, whether we shall be successful in this policy in the face of the well-known endeavours of certain competing firms to drive up the prices to an impracticable level. The tables on pp. 90 and 91 give particulars of the movement in prices, &c. at the last auctions in Mysore. The fact that last year almost all the oil distilled by us contained 94 p.c. of santalol, shows how carefully we proceed in buying sandalwood, and how excellent are our manufacturing arrangements.

The shipments of East Indian sandalwood from the Dutch East Indian Archipelago in the year 1913 have again declined. According to the Macassar statistics they have been as follows:—

1913 . . .	6451 piculs	1908 . . .	11309 piculs
1912 . . .	7455 „	1907 . . .	4899 „
1911 . . .	12818 „	1906 . . .	4879 „
1910 . . .	13112 „	1905 . . .	3226 „ .
1909 . . .	13486 „		

It will be seen from the above that the reckless destruction of the trees about which we have reported in the past attained its height in the year 1909, and that the injurious effects of this practice are now beginning to make themselves felt by a serious decline in the shipments.

Several parcels of so-called sandalwood from Madagascar and Siam, as well as from New Caledonia and other islands in the Pacific Ocean, which had been sent over, chiefly to France, in view of the advance in the price of sandalwood, have turned out to be unsuitable for distilling and have caused much disappointment to their owners.

As recently as in our last *Report* (p. 98) we mentioned a case of adulteration of sandalwood oil with glycerol acetate, and we are now again able to record another similar case. As in the previously-recorded instance, the sample was adulterated to to the point of being unrecognisable: $d_{15°}$ 1,0316, α_D — 9° 9′, acid v. 2,7, ester v. 221,6, soluble in 3 vols. a. m. of 70 p. c. alcohol. The quality of the oil may be judged without further examination from its excessive specific gravity and its abnormal ester value, which would correspond to a santalyl acetate content of over 100 p. c.

The glycerol ester was removed from the oil by extracting with 5 p. c. alcohol, and was identified from its constants after the separation of the solvent. It boiled at 3,5 mm. press. between 117 and 119°, its specific gravity was 1,1784 (15°) and its ester value 665. It therefore appears to consist chiefly of diacetine.

It is to be inferred both from the specific gravity and from the ester values of the oil before and after extraction with 5 p. c. alcohol that the addition of adulterant amounted to no less than 25 p. c.

From the Imperial Institute in London we have received three samples of different sandalwood oils which are of special interest because they were produced in the island of Mauritius. Two of the samples were distilled from heart-wood, the third from sap-wood. As will be seen from the subjoined table, all three were distinguished by their high santalol-content, and their other characters also agreed with those of East Indian oil, except that the optical rotation was a little higher: —

Colour	$d_{15°}$	α_D	$n_{D20°}$	acid v.	ester v.	Ester-santalol	Ester v. after acet.	Total santalol
Heart-wood, pale	0,9786	— 21° 50′	1,50698	1,9	5,6	2,2 %	207,2	96,4 %
„ „ dark	0,9816	— 20° 55′	1,50651	1,9	5,6	2,2 %	207,2	96,4 %
Sap-wood, pale	0,9808	— 21° 15′	1,50670	1,9	5,6	2,2 %	206,2	95,8 %

All the samples made a clear solution with 3,5 vols. a. m. of 70 p. c. alcohol.

Sandalwood Oil, West Indian. Thanks to the excellent position in which we are situated for procuring sufficient quantities of wood, we have been able to meet to the full the extraordinarily sustained demand during the winter months. Large transactions have been carried through in all the selling markets at prices which exceeded those of the first half year of 1913. The position of the West Indian sandalwood market is very firm, and customers who desire to benefit from our cheap stocks will do well not to wait too long. In the year 1913 we worked up about 300 tons of West Indian sandalwood, but at the moment we only have a moderate stock of oil available.

Sarsaparilla Root Oil. F. B. Power and A. H. Salway[1]) have obtained 0,01 p. c. of essential oil from sarsaparilla roots derived from various species of *Smilax* (N. O. *Liliaceæ*). The oil occurred as a yellowish liquid with a pleasant odour: b. p. 70 to 200° (15 mm.), $d^{15°}_{15°}$ 0,977, not completely soluble in 70 p. c. alcohol. The oil contained furfurol, and gave a blackish-blue colouration with ferric chloride, which points to the presence of a phenol.

Sassafras Oil. There is nothing new to report about this oil; the prices have remained unchanged and no alteration in the tendency of the market appears to be in prospect.

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[1]) *Journ. chem. Soc.* **105** (1914), 205.

Sandalwood-Auctions 1913.

Description	Tirthahalli	Sagar	Shimoga	Tarikere	Chikmagalur	Hassan	Bangalore	Seringapatam	Hunsur	Fraserpet	Total
	Nov. 17 1913	Nov. 20 1913	Nov. 24 1913	Nov. 27 1913	Dec. 1 1913	Dec. 4 1913	Dec. 8 1913	Dec. 11 1913	Dec. 15 1913	Dec. 17 1913	
	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons	Tons
2nd Class Billets . . .	1	—	7½	1	2½	2½	2½	5	5	10	37
3rd „ „ . . .	10	—	5	—	2½	—	—	10	2½	5	35
Ghotla	2½	—	—	5	2½	2½	—	5	2½	—	20
Ghatbadala	5	20	50	30	50	5	10	10	20	25	225
Bagaradad	—	5	7½	2½	5	5	2½	5	5	12½	50
1st Class Roots	10	15	15	2½	15	10	10	5	15	10	107½
2nd „ „	10	5	10	—	5	5	5	5	20	5	70
3rd „ „	7½	2½	5	7½	2½	2½	5	5	10	5	52½
1st „ Jugpokal . . .	40	25	50	50	40	15	25	30	40	20	335
2nd „ „ . . .	15	5	10	10	5	5	5	15	15	10	95
Ain Bagar	7½	5	5	7½	2½	2½	—	5	5	5	45
Cheria	2½	2½	—	—	—	—	—	—	2½	—	7½
Ain Chilta	10	5	10	25	15	5	5	10	20	2½	107½
Hatri Chilta	—	—	—	—	—	—	—	—	—	—	—
Milwa Chilta	25/30	20/25	40/50	25/30	30/40	10/15	10/15	30/40	30/40	25/30	280
Basola Bukni	12½	5	15	—	10	5	10	15	10	15	97½
Total	161	117½	235	168½	192½	77½	92½	160	207½	152½	1564½

Comparative prices obtained at the Sandalwood-Auctions of 1912 and 1913.

Prices realized:	Tirthahalli		Sagar		Shimoga		Tarikere		Chikmagalur		Hassan		Bangalore		Seringapatam		Hunsur		Fraserpet	
	16/12 1912	17/11 1913	12/12 1912	20/11 1913	9/12 1912	24/11 1913	5/12 1912	27/11 1913	2/12 1912	1/12 1913	28/11 1912	4/12 1913	25/11 1912	8/12 1913	21/11 1912	11/12 1913	18/11 1912	15/12 1913	16/11 1912	17/12 1913
	cif. d. w. p. cwt.		cif. d. w. p. cwt.		cif. d. w. p. cwt.		cif. d. w. p. cwt.		cif. d. w. p. cwt.		cif. d. w. p. cwt.		cif. d. w. p. cwt.		cif. d. w. p. cwt.		cif. d. w. p. cwt.		cif. d. w. p. cwt.	
2nd Class Billets	—	101/–	—	—	97/9	109/8	90/6	—	—	107/9	82/6	105/–	69/10½	106/9	62/6	105/9	58/6	102/–	61/6	102/9
3rd „ „	—	110/–	—	99/6	99/9	108/3	90/9	111/–	—	—	—	108/3	—	107/–	—	106/–	60/–	—	62/4½	101/9
Ghotla	—	108/9	—	—	—	106/–	92/9	—	—	108/6	—	107/8	—	—	—	105/9	—	102/3	—	—
Ghatbadala . . .	99/6	110/9	97/–	101/–	97/9 to 99/–	102/–	93/9	98/–	87/10½ to 88/3	98/6	82/3	98/3	73/–	—	64/–	—	59/7½ to 60/7½	98/9	59/6	93/3
Bagaradad . . .	—	107/9	—	97/–	91/6	100/3	86/3	96/6	—	—	83/6	—	—	—	—	—	61/9 to 62/3	—	57/7½	93/–
1st Class Roots	99/6	111/–	97/–	102/–	99/9	106/9	104/9	108/6	95/3 to 95/7½	108/–	84/6	107/9	81/3 to 82/–	107/3	69/3	105/9	66/3 to 67/3	105/6	62/3	—
2nd „ „	99/6	113/3	96/3	—	108/6	109/9	107/3	108/–	97/–	108/6	85/–	—	82/3	—	68/6	105/9	69/6	105/–	64/6	—
3rd „ „	99/6	108/–	92/6	—	104/6	108/9	—	108/9	—	104/–	79/3	—	74/3	—	—	105/–	68/6	107/6	61/–	104/3
1st „ Jugpokal	98/–	113/3	96/9	96/3	102/3	96/–	94/3	89/6	87/7½ to 88/6	90/9	82/6	—	81/–	—	66/3	88/3	61/9	89/3	59/9 to 60/9	89/6
2nd „ „	96/6	112/3	95/9	92/3	105/6	95/–	94/3	89/–	89/3 to 89/10½	—	82/3	—	81/9	—	65/3	86/6	59/9 to 60/1½	87/–	59/7½	87/6
Ain Bagar . . .	—	84/9	—	87/3	92/9	90/–	81/–	87/9	—	87/–	—	—	—	85,9	66/–	86/–	60/–	85/3	58/4½	88/–
Cheria	—	74/6	—	80/–	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Ain Chilta . . .	61/6	61/9	58/–	54/9	62/–	62/9	60/– to 62/3	64/6	59/–	62/–	59/–	—	52/6	60/–	47/–	60/9	48/3	69/9	46/9	61/9
Hatri Chilta . .	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Milwa Chilta . .	54/–	54/3	51/–	—	56/–	52/3	58/3	53/6	51/9	53/–	49/4½	53/–	46/–	52/6	39/–	51/–	37/–	47/6	36/9	48/6
Basola Bukni . .	39/–	48/–	37/6	—	43/–	48/6	41/9	48/6	42/3	47/–	44/10½	47/–	45/–	46/–	31/3	42/9	29/9	44/9	32/–	44/9

Savin Oil. After a prolonged period of interrupted supplies we have at last succeeded in discovering a few wagons of raw material of good quality at advantageous prices, and we have therefore been able to resume the distillation ourselves. Our own oil is prepared with the most up-to-date plant and compares favourably with the oil distilled abroad.

Shiu Oil. The German Consul at Kobe[1]) reports on shiu oil, which is related to linaloe oil, but is by no means equal to it in value. According to a communication by the Monopoly Bureau at Kobe, the oil is said to be prepared in Japan at the present time at the rate of from 1500 to 1600 lbs. per month. Formerly two grades of the oil were differentiated, namely A (decamphorised) and B (containing camphor), but at present only the B grade is still being prepared. The colour of this oil, however, varies from water-white to a somewhat clearly-defined yellow. The output, it is said, could be increased if the demand should warrant it; almost the whole of it is sent abroad in the unrefined state. One Japanese firm, according to its own statements, exported last year about 20 000 lbs. of the oil. The selling-price in London could not be ascertained in Kobe.

It is a remarkable fact that we have been unable to discover what becomes of these fairly considerable quantities of shiu oil in Europe.

Spearmint Oil. According to the information gathered by our New York firm the last crop has yielded about 10 000 lbs. of oil more than that of 1912. The increase in consumption, however, is equal to this surplus, and any reduction in prices during the summer therefore appears to be out of the question. The stocks which are still left are in the hands of firms with sufficient capital, which will of course take care to keep up the market. Since the beginning of the present year the turnover has only been small.

Spike Oil. When it was discovered that the crop had failed owing to the drought, pure French oils reached a price of from 14.— *fcs.* to 15.— *fcs.* But as, of course, at these fancy prices it was only possible now and then to find buyers among those who use the oil "for certain purposes", and were therefore not compelled to buy economically, business was restricted within very modest limits. Spain has supplied large quantities of excellent oil, possessing similar properties as the French oil, but here also, owing to the brisk demand from the South of France, the prices were run up to a considerable extent. At present the market is firm for qualities above reproach, but oil which has been adulterated with oils of camphor and rosemary can, as is always the case, be had at any desired figure, and many firms seem to regard it as a point of honour to supply their customers with such concoctions (which each customer could manufacture more cheaply for himself), under a guarantee of purity.

Star Anise Oil. During the past six months the prices of oil with a high sol. pt. have ranged round about 5/3 p. lb., and the trade for current requirements was generally very brisk. Only quite lately has the market begun to sag a little, as the arrivals from the interior of China have greatly increased, and as neither in Europe nor in the United States there is any trace of strong desire to buy. As a result the

[1]) *Nachr. f. Hand., Ind. u. Landw.* **1914**, No. 3.

prices have gone down to about 4/11 p. lb. Unfortunately that portion of the last crop of Tonquin star anise oil which still remains unsold is held for such a high price that it does not pay to use it it in the place of Chinese oil.

We advise, moreover, great caution in the purchase of this article, for our friends inform us that there are oils on the market which, while possessing the normal sol. pt. of 15°, are partly abnormal in respect of their other properties, and appear to be adulterated. The nature of the adulteration is not stated, but it may perhaps consist again of additions of fatty oil or mineral oil, such as have already been observed in the past[1]). Such sophistications are recognizable by their poor solubility; a genuine star anise oil gives a perfectly clear solution with $1^1/_2$ to 3 vols. a. m. of 90 p. c. alcohol.

According to a report by the Consul-General of the United States in Hong Kong[2]) the value of star anise oil in 1913 moved in sympathy with that of cassia oil, the quotations being as follows: January $ 390.— local currency (= $ 197.— gold) per picul, May $ 410.— local currency (= $ 200.— gold) and at the close of the year $ 335.— (= $ 164,15 gold), the last-named being the bottom price of the year. So far as the Hong Kong market is concerned, the principal producing centre of both oils is the Province of Kwang-si.

The value of the exports of star anise oil to the United States in 1913 was $ 93199, as compared with $ 92138 in the year 1912.

A. Chevalier[3]) communicates interesting particulars on the cultivation of, and trade in, star anise in Tonquin. The parent-plant of star anise, *Illicium verum*, Hook. f. (N. O. *Magnoliaceæ*), is a small evergreen tree, growing to a height of from 8 to 15 metres, and resembling the cypress in its outline. The tree flowers twice a year. There are several varieties of *Illicium verum* and in view of their possible economic utiliration it would be interesting to investigate them. It is very doubtful whether the star anise tree is found in the wild state; it is cultivated in the South of China, especially in the Province of Kwang-si and on the Island of Hainan. In Tonquin it is cultivated within a radius of from 20 to 30 kilometres of Lang-son[4]). The tree requires a very special climate, and this is the reason why its habitat is rather restricted. In the districts where the star anise tree flourishes the annual rainfall is about 1,50 m. Between April and July the temperature is very high, often as much as 40° C., August and September are cooler, with frequent rains, in October the weather is cool but dull and in December and January the thermometer often falls as low as 5° C., and at times even below freezing point. Then the air is very humid, and at this period mist or fine rain is not at all rare.

The star anise tree prefers slopes with a soil of red clay mixed with slate. The best site for a star anise plantation is a forest-soil which has been made arable. The seeds soon lose their power of germinating, and if they are not sown at once it is well to preserve them in layers in dry earth. They germinate best in a covered nursery, which should be protected against the hot rays of the sun. During the dry season the young plants require watering, and when a year old they are planted out on the same site. The holes in which they are to be planted are dug out a long time beforehand, and should be at distances of 5 or 6 m. in crosswise rows. It is necessary

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[1]) Comp. *Report* April **1912**, 120; October **1912**, 105. — [2]) *Daily Cons. and Trade Rep.*, Washington **17** (1914), No. 56, p. 906. — [3]) *Journ. d'Agriculture tropicale* **14** (1914), 40. — [4]) See the illustration at p. 399 of Gildemeister and Hoffmann's *Die ätherischen Öle*, 2nd Ed. Vol. II.

to leave a few shade-trees in the plantations. Until its eighth or tenth year the star anise tree requires to be tended very carefully, and suitable manuring is of great advantage for its proper development. The trees only bear for the first time when they are from 10 to 15 years old; they yield their most abundant crops between the ages of twenty and thirty-five years, but it is said that there are century-old trees which are still bearing. It is difficult to state the average yield of a tree, because some of them bear fruit almost throughout the year, while others bear very scantily. A plantation of one hectare (2 1/2 acres) does not yield more than 5 tons of green fruit in a good year.

The fruit which is intended for distilling must be gathered before it is quite ripe. The collectors use bamboo-ladders and gather the fruits by hand. The principal crop is collected in August and September, and a second crop in February and March. Crop-failures are attributed chiefly to unfavourable climatic conditions. The tree also suffers from various diseases and from the ravages of insects, but nothing definite is known on this subject. A small beetle, resembling a lady-bird in appearance, devours the leaves, and white ants frequently attack the bark; the larvæ of insects which are found in the branches also do a good deal of damage.

The fruits, when gathered, are distilled at once in primitive but very cleverly constructed stills of Chinese origin. The oil-yield varies from 1,7 to 3,5 p.c. according to whether the fruit is dry or wet; with modern apparatus it would presumably be possible to obtain a yield of 5 p.c.

The establishment of a central distilling-plant at Lang-son, which has already been proposed, does not seem practicable to Chevalier, because the roads there are in a bad state and the transportation of the raw material would therefore be attended with difficulties. In his view the most rational plan would be to set up small modern stills locally; it would then also be possible to distil the star anise leaves, which is even now done in the neighbourhood of Lang-son when the crop has been poor. It is said that the oil-yield of the leaves is only half of that of the fruits. The middlemen who buy up the oil are said to make little difference between that from the fruit and the leaves.

The annual output of star anise oil in Tonquin varies greatly. In 1894 it was 23 tons, in 1900 45 tons, in 1902 58 tons, in 1904 66 tons, in 1911 100 tons and in 1912 46 tons.

Until about 12 years ago the Tonquin star anise oil was bought up by Chinese. To-day this work is done by a French firm, and the oil is exported via Haiphong instead of via Canton, as formerly.

Since the year 1896 an export duty of 200 *fcs.* per 100 kilos is levied upon star anise oil which is exported from Tonquin over the Chinese frontier, and since that time the star-anise plantations have been free from taxation, with the result that their number has greatly increased in Tonquin. In the year 1913 5000 cases, each of 4 tins of 7 1/2 kilos were exported, the value being 2 500 000 *fcs.*, as compared with 3000 cases exported from China. Tonquin star anise oil is chiefly shipped to Havre and Marseilles, partly also to Hamburg.

Tansy Oil. Our New York branch house reports that the crop has only been a small one and the prices have therefore correspondingly advanced. Further increases in price are in prospect, because it will take two years before the area which has been newly put under tansy this spring is capable of producing a crop.

Turpentine Oil. The Government of India is at present engaged, at its turpentine-distilling plant at Naini Tal, in the Himalayas, on experiments in the more rational preparation of the oil[1]). It is true that the turpentine oil which has thus far been manufactured in the United Provinces is colourless, but it contains sparingly-volatile bodies, as a result of which it dries but slowly, and leaves a sticky residue. It is expected that, hand in hand with an improvememt in the quality of the product, there will be a considerable increase in the output within the next few years. The production of the last three years has been as follows: —

Year	Number of Trees	Crude Turpentine lbs.	Turpentine oil Gallons	Resin[2]) lbs.
1910/11	194 000	1 150 000	25 200	780 000
1911/12	213 000	1 400 000	30 000	990 000
1912/13	400 000	2 470 000	54 000	1 650 000
Estimated output for the financial year 1916/17 . .	900 000	5 760 000	126 000	3 870 000

The total output of resin in British India in the year 1912 was 1 890 000 lbs.; that for 1913 is estimated at 3 290 000 lbs., of which over 2 000 000 lbs. has already been forwarded to Calcutta and Bombay. A new distillery is about to be put into commission at Tanakpur and the Government experimental plant at Lahore (Punjab) is to be got ready for regular work as soon as possible.

As long ago as our *Report* of April **1911**, p. 116, we called attention to the fact that, owing to its sylvestrene-content, Indian turpentine oil from *Pinus longifolia* lacked the valuable drying properties of the French and American turpentine oils, which consist almost entirely of pinene.

A few years ago, Engler and his collaborators showed that under the influence of aluminium chloride, amylene is polymerised into polyolefinenes, which afterwards are split up into paraffins containing larger proportions of hydrogen, into naphthenes (*cyclo*-hexanes) of the same percentual constitution and into lubricating oils containing less hydrogen. W. Steinkopf and M. Freund[3]) have ascertained that French turpentine oil and pure *l*-pinene behave similarly. When turpentine oil without any other diluent is diluted with freshly-prepared aluminium chloride, it is necessary to proceed with extreme care, or the reaction, with spontaneous heating, will proceed so violently that resinous masses will be hurled from the flask to the accompaniment of a pronounced evolution of smoke. When the aluminium chloride is introduced gradually, with cooling and turbinating, a liberal yield is obtained of a viscous mass consisting of the polymerisation-products of pinene. In order to decompose these products they were heated in a reflux condenser with aluminium chloride. This manipulation gave rise to gases, to hydrocarbons with low b. p. and to fractions with higher b. p. The gases consisted chiefly of saturated hydrocarbons of the paraffin series, with which were admixed cyclic hydrocarbons and a minute proportion of unsaturated hydrocarbons. The high-boiling fractions contained in addition to a little benzene chiefly naphthenes and polynaphthenes, together with other saturated hydrocarbons. The constitution of the fractions with the highest b. p. was similar to that of the various artificial and natural lubricating oils.

[1]) *Zeitschr. f. angew. Chem.* **27** (1914), III. 91. — [2]) Colophony? — [3]) *Berl. Berichte* **47** (1914), 411.

From the turpentine of *Cedrus Libanotica*[1]), L. Reutter[2]) has prepared an essential oil by steam distillation in the presence of potassium hydroxide. The oil possesses the following properties: $d_{15°}$ 0,8802, α_D — 13° 36′, $n_{D20°}$ 1,48567. It contains borneol (m. p. 203°).

In another publication, Reutter[3]) refers to turpentine oil from *Pinus brutia,* Ten., which also contains borneol. He obtained about 16 p.c. of this oil from the turpentine.

A. W. Schorger[4]) reports on the resin of the "Jeffrey" and "Single leaf pines" (*Pinus Jeffreyi,* A. Murr. and *P. monophylla,* Torr.). The turpentine from *Pinus monophylla* contained 19 p. c. of a volatile oil possessing the following characters: $d_{15°}$ 0,8721 to 0,8733, $\alpha_{D25°}$ + 14,41 to + 17,26°, $n_{D15°}$ 1,4732 to 1,4733. The oil distilled over between 155,9 and 190°. It contained about 80 to 85 p.c. *d*-α-pinene (nitrolpiperidine, m. p. 118°), also 4 to 5 p.c. *l*- or *i*-limonene (dihydrochloride, m. p. 49°) and from 4 to 6 p.c. *d*-cadinene ($\alpha_{D25°}$ + 10,58°; dihydrochloride, m. p. 117 to 118°). In the turpentine oil from *Pinus Jeffreyi* (yield 8,81 to 11,25 p. c.; $d_{15°}$ 0,6951 to 0,7110; $n_{D15°}$ 1,3927 to 1,4060) Schorger, corroborating Blasdale's statements[5]), found about 95 p.c. *n*-heptane, and in addition thereto about 5 p.c. of an aldehyde, b. p. 200 to 215°: $d_{15°}$ 0,8578, $\alpha_{D20°}$ — 2,5°, $n_{D20°}$ 1,4570. The semicarbazone had m. p. 91 to 92°. It was impossible, for want of material, to prepare other derivatives. Schorger suspects the aldehyde to be citronellal.

On p. 112 of our *Report* of October **1912** we reported on a control-test of Walbum's method of testing larch-turpentine (Venetian turpentine) which has been carried out by us. We advised against the making of claims based upon Walbum's test. S. C. Süntola[6]), who has made investigations with numerous samples of different samples turpentine, has arrived at the same conclusion as ourselves, namely that Walbum's method cannot be recommended for the examination of larch turpentine.

E. H. French and J. J. R. Withrow[7]), in a detailed article, pass into review the present state of the so-called wood turpentine industry[8]), which may safely be said to be very bad indeed. The authors give three reasons for this state of things: 1) the lack of practical, scientific engineers experienced in this or analogous fields; 2) financing for the sale of stock and securities rather than product. 3) Lack of efficient marketing organisation. Furthermore, the oil is prepared by many widely-different methods, so that no uniform product is supplied, which increases the cost of selling. Up to the present it is probable that sufficiently classified oils have been sold only to the U. S. Navy. So far those engaged in the industry have taken no interest in the establishment of a standard for wood turpentine, in spite of the fact that a few years ago the manufacturers who worked the steam-process, now almost obsolete, were making efforts in this direction.

The speculative movements of the Naval Stores market formerly were very favourable to the development of the wood turpentine industry. The prices of wood turpentine were fixed according to the quotations of gum turpentine oil; hence, so long as the turpentine oil prices rose or kept high, it was possible to lay down at great expense

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[1]) Presumably the Lebanon cedar, *Cedrus Libani,* Barr. is here meant. We cannot trace a *Cedrus Libanotica,* either in the *Index Kewensis* or in Beissner's *Handbuch der Nadelholzkunde,* II. Ed. Berlin 1909. — [2]) *Schweiz. Wochenschr. f. Chem. u. Pharm.* **51** (1913), 472. — [3]) *Ibidem* 492. — [4]) *Journ. ind. eng. Chemistry* **5** (1913), 971. The author has kindly sent us a reprint. — [5]) *Journ. Americ. chem. Soc.* **23** (1901), 162; *Pharm. Review* **25** (1907), 363. — [6]) *Pharm. Zentralh.* **55** (1914), 2. — [7]) *Journ. ind. eng. Chemistry* **6** (1914), 148. — [8]) Comp. Gildemeister und Hoffmann, *Die ätherischen Öle,* 2. Ed. Vol. II. p. 100.

wood turpentine distilleries with costly plant, and to exploit them successfully. Afterwards, when owing to interference by the Government an end was put to the excessive speculation, a reaction set in, and numerous wood turpentine distilleries were financially ruined.

For some time, owing to the high prices of turpentine oil, a great many more pine trees were tapped than formerly, with the result that later on over-production of turpentine oil made itself felt.

The authors give detailed particulars of the various methods of manufacturing wood turpentine. They enumerate the steam process, the solvent process, the alkali process, the bath process and the distillation process.

In the steam process the wood, after being broken up, is distilled by steam under pressure until only little oil passes over. This process is profitable only when turpentine oil prices are high.

The solvent process, in which the wood is treated either before or after distillation by steam with a volatile solvent has the drawback that too large a proportion of the extracting-agent is lost.

The alkali process is protected by numerous patents. It is applied where the wood is made into paper, and where the wood turpentine products are recovered only as by-products. This process requires somewhat expensive apparatus.

In the bath process the wood is heated in retorts fitted with double jackets within which the high-boiling turpentine products, heated to a high temperature, circulate. The wood turpentine obtained by this process is of good quality, although not so good as the product prepared by the steam process. The great waste of fuel, presumably owning to the formation of highly-volatile decomposition-products, makes the process little profitable.

The distillation process is based upon the dry distillation of the wood, and appears to have the best financial prospects. The authors distinguish three varieties of this process, which it would lead us too far to discuss, in particular because we have already repeatedly dealt with the manufacture of wood turpentine[1]).

In continuation of a paper published by him some years ago[2]), O. Aschan[3]) has examined the first runnings of a Finnish pine-tar oil. He used as his raw material a substance which had been distilled from the crude pine-tar oil by steam, without the addition of lime, in the year 1906. At the time this product had d_{15° 0,8720, but in 1912 it had d_{15° 0,8965, an increase which indicated very considerable condensation of the unsaturated constituents.

Aschan states that this material, in addition to acetone, contained the following constituents: furane, sylvane, acetaldehyde and propionic aldehyde.

In the same paper Aschan refers to the theory of wood-distillation. He suspects that the bodies which are present in the first runnings of pine-tar oil are not generated from the resins and terpenes but from the ordinary wood-substances. For particulars of his detailed explanations we must refer to the original.

Vetiver Oil. Excellent material for distilling has again been available, and we have therefore no longer to fear the competition of the cheaper Réunion oil. The

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[1]) Comp. *Report* October **1907**, 94; November **1908**, 125; October **1909**, 119; April **1910**, 118; April **1912**, 126; October **1912**, 110; April **1913**, 105. — [2]) *Zeitschr. f. angew. Chem.* **20** (1907), 1811; *Report* April **1908**, 105. — [3]) *Zeitschr. f. angew. Chem.* **26** (1913), I, 709.

shipments from Réunion amounted in 1913 to about 1891 kilos, compared with about 1421 kilos in the year 1912. The fact that, in spite of this increase in the output, the price was maintained at about 75.— *fcs.* instead of dropping back to somewhere near its old level of 30.— *fcs.*, proves, we should say, that the value is kept up artificially, for in our opinion it is hardly probable that there has been any increase in the consumption.

Oil of Wallflower Seed. W. Schneider[1]), in collaboration with A. Schütz, has continued his researches into the glucoside of cheiroline, the *iso*sulphocyanate of wallflower seed[2]). In the course of these he has been successful in preparing the glucoside, called glucocheiroline, in a chemically pure form. This body constitutes small, very slightly hygroscopic needles, m. p. 158 to 160°, possessing the chemical formula $C_{11}H_{20}O_{11}NS_3K + H_2O$, and consequently is a complete analogue of sinigrin. Exactly like the last-named it is readily split up by the enzyme myrosine, affording cheiroline; when boiled in a hydrochloric acid solution with barium chloride it gradually splits off quantitatively one molecule of sulphuric acid; with silver nitrate in aqueous solution it affords a silver compound analogous with sulphocyanate-silver sulphate: cheiroline silver sulphate, of which the constitution is $C_5H_9O_2NS_2$, $Ag_2SO_4 + H_2O$. One molecule of *d*-glucose is split off during the reaction. This silver compound, when boiled with aqueous solutions of chlorides, readily affords cheiroline. Basing themselves upon these reactions, Schneider and Schütz assign to cheiroline a similar constitution to that which Gadamer had made probable for sinigrin; a composition which may represented by the formula $CH_3 \cdot SO_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot N : C \begin{matrix} S \cdot C_6H_{11}O_5 \\ O \cdot SO_2 \cdot OK \end{matrix}$.

With the object of obtaining the glucoside, the authors extract wallflower seed from which the fatty constituents have been removed, with alcohol, the impurities being abstracted from the alcoholic solution by careful treatment with lead oxide and lead acetate. Glucocheiroline dissolves very readily in water, but only traces of it can be dissolved in hot absolute alcohol. Optically it is lævorotatory: $[\alpha]_{D\,27°}$ — 21,09 to — 21,56° in aqueous solution. The water of crystallisation adheres most persistently and only disappears after several days' heating *in vacuo* at 15 mm. over phosphorus pentoxide to 98°.

In contradistinction to sinigrin, which is bitter, glucocheiroline is quite tasteless.

Wintergreen Oil. The prices have now been stable for a long time, and so far as it is possible to form a judgment from the reports of our New York branch house, no alterations are to be expected.

We learn from an English periodical[3]) that the Bureau of Chemistry of the United States has discovered a method which is said to enable it to detect the addition of synthetically manufactured methyl salicylate in the natural product. Up to the present no particulars whatever of the test have been published, as the applicability of the method in practice is still being tested.

In the same journal[4]) the following colour test is published for the detection of the addition of synthetic methyl salicylate to natural wintergreen oil: to five drops of the oil in a test tube add five drops of a 5 p.c. alcoholic solution of vanillin and 1 cc.

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[1]) *Berl. Berichte* **46** (1913), 2634. — [2]) Comp. *Report* April **1913**, 107. — [3]) *Perfum. Record* **5** (1914), 4. — [4]) *Ibidem* 60.

of alcohol. Shake well, and add 2 cc. of concentrated sulphuric acid and mix thoroughly. When this test is applied, pure Gaultheria oil produces an intense crimson colour, and pure Betula oil a deep blood red, while synthetic esters give a yellow colour. The author of the article concludes from the above that this test will make possible the differentiation of pure natural oil from oil which is heavily adulterated with the artificial product, but he very properly leaves it an open question whether the test will prove to be really useful in practice.

We have made a control-test with oils distilled by ourselves, and have generally confirmed the statements made above, except that we found that Betula oil at first gave a decidedly paler colour than did Gaultheria oil. In the course of time the colours of both oils assumed the same dark tone, and in the end scarcely any difference was perceptible. The synthetic product produced the yellow colour mentioned above.

Wormseed Oil, American. Fortunately, the fears which we felt last autumn in respect of the result of the crop have not been realized. When the distillation began in the autumn of 1913, large quantities of oil from 1912 were still available, and second-hand holders also were plentifully supplied. As a result of these conditions the prices began to give way, and as the farmers in Maryland could not make up their minds to accept the bids made them by the dealers, they will in all probability be obliged to continue to carry their stock for some time to come. In Europe the excellent medicinal qualities of American wormseed oil are continually causing an extension of the demand, and we are of opinion that the future of the article is full of promise.

A. Lechler, in a dissertation[1]) describes the excellent action of American wormseed oil, as well as of Wermolin *(Emulsio olei chenopodii anthelmenthici composita)*, a preparation from this oil, in the treatment of ascaridæ. It appears from Lechler's investigations that ascaridiasis is a very frequent complaint with children, and that its seriousness should not be underestimated.

We are now able to give some furtner particulars of Wermolin, which we take from a paper[2]) by Brüning which, although published some considerable time ago, has only just come to our knowledge. The disagreeable taste and odour of American wormseed oil have always been an inducement to try to find a suitable form of administering it. As capsules are out of the question, especially for juvenile patients, the obvious alternative appeared to be to render the oil less unpleasant to the taste by suitable aromatisation, but in spite of many attempts no such suitable method has yet been found. Better results were achieved by giving the oil as an emulsion, and such a preparation has been sold for many years by the "Adler"-pharmacy at Hilden, (Rhine-Province) under the name of Wermolin. The mixture is put up in vials of 50 grams and sold at ℳ 1,50 per vial. The sole active principle of the mixture is 1,5 grams per vial of American wormseed oil in castor oil, saccharin and essential oils being used to correct the taste. The dose, according to the instructions, varies for children from a teaspoonful to a tablespoonful according to age, morning and evening; for adults the dose is a full vial, divided in two equal portions to be taken in the course of one day. The principal function of Wermolin is to expel ascaridæ, but it

[1]) *Zur Frage der Häufigkeit, Diagnose und neueren Behandlung der Spulwurmkrankheit bei Kindern* (On the frequency, diagnosis, and modern treatment of ascaridiasis in children), Rostock 1913. From a copy kindly sent to us. — [2]) *Deutsch. Med. Wochenschr.* **38** (1912), 2368.

is said that in the form of an enema (one part of Wermolin to four of glycerine and water), it is effective for threadworm.

Experiments with Wermolin made by Brüning on children between the ages of 2 and 14 confirm the efficacy of the remedy. Children of all ages take the emulsion without trouble, in the required dose, although the peculiar strong odour and taste of the wormseed oil are not covered in any marked degree. In every case the remedy was effective. It is advisable to give an aperient (castor oil or "Laxine" tablets) about two hours after the last dose of Wermolin. Brüning thinks that the remedy is probably effective also in threadworm, but he has made no observations in regard to this.

Prof. R. Kobert of Rostock has written to inform us that he has succeeded in detecting the presence of two saponin-bodies in the herb and the seeds of *Chenopodium ambrosioides*, L. var. *anthelminticum*, Gray as well as in other plants belonging to the N. O. *Chenopodiaceæ*, such as sugar-beet and spinach. Of these two, the acid saponin body, which has a powerful action upon the blood, occurs in considerable proportions. This discovery is of particular interest inasmuch as the anthelmintic action of the powdered drug is due to these saponin-bodies as well as to the essential oil. Kobert suspects that these bodies are found in the leaves and are then deposited in the seeds, and that this apparently applies not only to *Chenopodium* but to all the representatives of the Family of the *Chenopodiaceæ*. Where tubers are present, the saponin-bodies are also deposited in them.

Wormwood Oil. According to the report supplied by our New York friends the last crop, owing to the dry weather which prevailed, has been smaller than that of 1912, but as the consumption in many of the former markets has been greatly reduced owing to legislative measures, large stocks, estimated at not less than two-thirds of the total yield of the crop, have accumulated both in the West and in New York. It will be necessary to abate the quotations considerably if this excess of wormwood oil is to be liquidated before the next crop comes in. Our own German wormwood oil from herb grown at Miltitz is in better demand than the American oil, and the supplies of it which are still available may be just sufficient to hold out until the arrival of the new crop.

Ylang-Ylang Oil. The sale of our "Sartorius" brand, which continues to receive the preference, and to lead the market in respect of quality, has been normal, but in the prevailing conditions it is difficult to find new customers for the article, the reason being that the superiority of our brand usually only makes itself perceptible in the finished perfumes. Hence it is natural that the cheap Réunion- and Madagascar-oils which are being offered from France constitute a great temptation to discard the Manila oil. Unfortunately the statistics published by the Chamber of Commerce of St.-Denis no longer give particulars from which the exports of Réunion oil can be seen, but to all appearance the total for 1913 was about the same as that for 1912.

In the *Jahresbericht* of the Biological-Agricultural Institute of Amani[1]) for April 1912 — 13 we find a notice relating to the distillation of ylang ylang flowers[2]) which has been carried out there. The distilling-plant available at Amani is very unsuitable for the purpose, because it is bricked-up at the laboratories, at a distance of about

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[1]) *Der Pflanzer* **10** (1914), 32. — [2]) Comp. *Report* October **1911**, 102.

45 minutes from the plantations. Moreover, the apparatus is so constructed that it is impossible to avoid contact of the flowers with the hot water, while fractional collection of the distillate is difficult and cannot be done completely. A first experiment, which was made at the beginning of the year under review with 77,5 kilos of flowers, several separate charges being made, afforded 0,75 p.c. of oil. During the carriage from the plantation to the plant the flowers, even when loosely packed in large baskets, unavoidably became somewhat heated and faded. The experiments made at the end of the year under review gave the following results: —

25. III. 13	19,4	kilos	flowers,	Time	of	dist.	2	hours,	yield	1,2	%	pale	green oil,
26. III. 13	32,7	„	„ ,	„	„	„	2	„ ,	„	0,55	%	„	yellow „ ,
27. III. 13	35,4	„	„ ,	„	„	„	2	„ ,	„	0,51	%	„	„ „ ,
28. III. 13	14,1	„	„ ,	„	„	„	1	„ ,	„	0,41	%	„	„ „ ,
29. III. 13	16,5	„	„ ,	„	„	„	1	„ ,	„	0,15	%	„	„ „ .

A sample of ylang-ylang oil distilled in the island of Mauritius which has been sent to us for our opinion by the Imperial Institute in London, showed the following constants: $d_{15°}$ 0,9906, α_D — 29° 18′, $n_{D20°}$ 1,50790, acid v. 1,9, ester v. 181,1, soluble in 90 p. c. alcohol up to 1,5 vols. Turbidity ensues when more of the solvent is added. In spite of its high ester-content, chiefly represented, judging by the odour, by benzyl acetate, the oil does not compare in respect of aroma with good Manila brands, and must therefore be pronounced as of inferior quality. In view of the notorious overproduction[1]) of ylang-ylang, an oil of the character of that described above would be very unlikely to find a profitable market.

Novelties.

Ashanti Pepper Oil. The fruit of Ashanti pepper, *Piper guineense,* Schum. et Thonn. (N. O. *Piperaceæ*), a native of tropical Western Africa, contains an essential oil of which hitherto nothing was known. A sample distillation carried out by us with two small samples received from Mayumba[2]) should therefore be of general interest. The oil-yields were respectively 11,5 and 10,96 p. c. The oils were colourless to palish yellow, and had a peppery, and at the same time somewhat sweetish odour. For the rest their characters were as follow: —

	$d_{15°}$	α_D	$n_{D20°}$	acid v.	ester v.	ester v. after acet.	solubility in 90 p. c. alcohol
I.	0,8733	— 3° 43′	1,48905	0,6	5,5	—	Sol. in 8 vols. a. m. with turbidity
II.	0,8788	— 5° 34′	1,48847	0,9	4,2	22,1	Sol. in 8 vols. a. m.

Both samples gave a pronounced phellandrene-reaction.

From the fruit of *Piper Clusii,* C.DC., which is said to be a variety of *P. guineense,* and which was also designated as Ashanti pepper[3]), Herlant[4]) has obtained 11,5 p. c. of essential oil.

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[1]) Comp. *Report* October **1911**, 103; April **1912**, 135. — [2]) The botanical determination of the fruit was made for us by Dr. Giessler, curator of the Botanical Institute of University of Leipzig. — [3]) R. Sadebeck, *Die Kulturgewächse der deutschen Kolonien und ihre Erzeugnisse* (Jena 1899), p. 182. — [4]) *Acad. Roy. de Méd. de Belgique* **1894**, 115. Comp. Gildemeister and Hoffmann, *Die ätherischen Öle,* 2nd Ed., Vol. II, p. 309.

Oil from Cathetus fasciculata. *Cathetus fasciculata,* Lour. (*Phyllanthus cochinchinensis,* Muell.), a euphorbia which occurs in Southern China and in Cochin China, contains an essential oil of which a small sample reached us recently from Annam, where the plant is known by the name of *Bruyère d'Annam.* The oil was of a bluish-green colour, and possessed an odour reminding somewhat of cajuput oil. Its constants were as follow: $d_{15°}$ 0,8897, α_D — 4° 34′, $n_{D20°}$ 1,47544, acid v. 1,9, ester v. 3,7, ester v. after acet. 44,8 = 12,7 p. c. $C_{10}H_{18}O$, soluble in 0,5 vol. a. m. of 90 p. c. alcohol; not even 10 vols. of 80 p. c. alcohol were sufficient to make a solution. Among the constituents is to be mentioned cineol, which was identified from the iodol-compound (m. p. 112°). Judging by the odour of the oil, cymene and linalool are also present.

A sample of oil sent to us many years ago under the name of "Essence de Bruyère du Tonkin" possessed precisely similar characters, with the exception of the rotation; $d_{15°}$ 0,8787, α_D + 10° 32′, $n_{D20°}$ 1,47009, acid v. 1,7, ester v. 5,9, ester v. after acet. 45,2, sol. in 0,3 vols. a. m. of 90 p. c. alcohol. Here, also, we were able to identify cineol by the iodol test. We believe that we are not mistaken in regarding *Cathetus fasciculata* as the parent plant of the last-named oil also.

Another sample of "Essence de Bruyère" was mentioned in our *Report* of April **1904**, p. 97.

Machilus Oil. We have received under this name from Japan a small quantity of oil distilled in that country. The oil constituted a solid, yellowish mass, and in this respect, as well as in its colour and odour, it reminded of guaiacum wood oil, although it does not compare in any degree with the latter in regard to aroma. It did not melt below 58°, and then formed a yellowish liquid.

The other characters of the oil were as follows: $d_{50°}$ 0,9482, $[\alpha]_D$ + 27° 50′ (in 10 p. c. alcoholic solution), acid v. 1,2, ester v. 5,4, ester v. after acet. 155,5, soluble in 3 vols. a. m. of 70 p. c. alcohol. By suitable treatment with acetone we succeeded in isolating the crystalline portion which constituted the bulk of the oil. After repeated crystallisation from 60 p. c. alcohol this portion was obtained in the form of white, matted needles of a silky lustre, m. p. 82°. The specific rotation, determined in a 10 p. c. alcoholic solution, was $[\alpha]_D$ + 38° 26′. It is obvious that the body constituted a sesquiterpene alcohol, for under heating with concentrated formic acid, water was eliminated.

We had received no information concerning the parent plant of the oil. It is probably *Machilus Thunbergii,* Sieb. et Zucc. (*Laurus indica,* Thunb.), a laurel which, according to J. J. Rein (*Japan nach Reisen und Studien,* 1886, Vol. II, p. 291), occurs on the southern islands of the Japanese Empire as well as along the coast from Hondo to Tokyo.

Oil of Pelargonium tomentosum. At the suggestion of Prof. Heckel, of Marseilles, we have received from the Botanical Gardens in that city a sample of herb of *Pelargonium tomentosum,* L. (N. O. *Geraniaceæ*). When distilled by steam, the herb afforded about 0,01 p. c. of an oil of a brownish-yellow colour with an aroma of menthone or pulegone. Unfortunately the sample consisted of only a few drops, and any further examination was therefore out of the question.

Chemical Preparations and Drugs.

Almond Oil, pressed, from Almonds (German Pharmacopœia V). The abnormal state of the sweet almond market has notoriously been due to the entire failure of the crop in Sicily, following a poor crop in the year 1912. Last year the Sicilian output only reached from 10 to 20 p. c. of the average, and in 1912 the yield was from one-half to two-thirds of a normal crop. In the face of these facts no further explanation is needed to account for the record-prices which prevailed in the year 1913. The highest figure, 285,50 ℳ per 100 kilos cif Hamburg, was reached at the end of December.

It goes without saying that, at such a fancy-price as 7,60 ℳ, buyers only showed a limited interest in our pressed almond oil, but in spite of this our stocks dwindled so rapidly as to compel us on several occasions to buy raw material at the high current prices. We see in this circumstance a proof of the excellence of our oil, which has become indispensable to many regular customers, not only among pharmacists.

Fortunately the prospects for 1914 are favourable, and as a result there are, since the middle of February, cheap quotations in the market for almonds of the season 1914. No reports have yet been received concerning the state of things prevailing in Apulia.

We are indebted to Messrs. Fratelli Jung, of Palermo, for the chart of the fluctuations in market-values during the period of high prices which will be found inserted between pp. 104 and 105, and we here express our thanks to them for this courtesy.

Almond Oil, pressed, from Apricot kernels. In view of the exceptional state of the almond-market, it is gratifying to be able to confirm the report that the apricot crop of 1913 in the district of Damascus (which furnishes almost exclusively the raw material pressed by us), has been very prolific. It was of course to be foreseen that prices would be well maintained, for by the time when the new crop was available practically no apricot-kernels from the previous year's crop were left. Moreover, not only California, but China also has ceased for the time to be a source of supply. In California the crop was a failure, and although in China considerable quantities were available, it was impossible to bring them to the coast, partly because the roads in the interior were blocked by snow, and partly as a result of the generally unsatisfactory conditions prevailing there. As soon as the shipment of the Chinese kernels begins, the price of Damascene apricot kernels will probably recede somewhat, unless, contrary to expectation, the whole of the Damascene supply should by then have passed into the hands of the consumers. During the winter there has been a very sustained demand for our pressed almond oil from apricot kernels, and as, in spite of our large output, we are never accumulating any stocks worth mentioning, it is probable that we shall be unable to lower our quotations for some months to come. Naturally, the unsatisfactory conditions prevailing in the almond market greatly assist the sale of oil from apricot kernels.

Benzoin. E. M. Holmes[1]) has published a synopsis of the references on the parent-plant of Siam benzoin which are scattered through literature. As we referred to this matter some time ago[2]), a mere mention of the article will here be sufficient.

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[1]) *Pharmaceutical Journ.* **91** (1913), 804. — [2]) Comp. *Report* April **1913**, 114; October **1913**, 116.

Bornyl Acetate. Among the samples of bornyl acetate which have recently been submitted to us for our opinion, one is deserving of special mention in this place, because it shows the kind of article which sellers occasionally have the temerity to offer for sale. The product in question, which had been sold by a Hamburg firm, and was deliberated described as "bornyl acetate, 100 p.c." was nothing but common Siberian pine-needle oil with an ester-content of 43,9 p.c. It was further differentiated from bornyl acetate by its lower specific gravity ($d_{15°}$ 0,9195) and by the fact that it was only soluble in 90 p.c. alcohol (0,5 vols a. m.). The specific gravity of 98 to 100 p.c. bornyl acetate ranges from 0,987 to 0,991, its ester value from 280 to 285, and it is soluble in about three times its volume and more of 70 p.c. alcohol.

Cinnamic Alcohol. In our opinion this very useful preparation is not by any means so well appreciated in the perfumery industry as it deserves. Its unobtrusive, hyacinth-like smell, is of great use in the preparation of all manner of perfume-compositions. We are equipped for its manufacture on the largest possible scale, and are able to offer special advantages for contracts of some magnitude. Our cinnamic alcohol is readily soluble in alcohol, it boils at about 257°, and its specific gravity at 35° is from 1,01 to 1,03. Its m. p. is between 32 and 33°.

Citral. The declining tendency of the price of lemongrass oil is naturally affecting in a corresponding degree the cost-price of citral, a preparation which is indispensable in the manufacture of violet-perfumes. We are therefore now able to offer citral at reduced prices, and we shall be pleased to submit special quotations for quantities of some importance. It would be superfluous to call attention to the high degree of purity of our preparation, but it is not amiss to point out that citral has been offered (particularly in the English market and, regrettably, from German sources), which consisted simply of a lemongrass oil fraction of which the intrinsic value scarcely exceeded that of rectified lemongrass oil.

Copaiba Balsam. The Netherlands Colonial Museum at Haarlem[1]) has received from Surinam two samples of copaiba balsam from *Copaifera guyanensis*, Desf. (N. O. *Leguminosæ*). One of the samples was cloudy, the other clear. The constants of the two were about similar: d 0,9659 and 0,9712, acid v. 70, sap. v. 84. The percentages of volatile oil were respectively 29 and 23,7.

Coumarin. A new synthesis of coumarin is described by H. Meyer, R. Beer and G. Lasch[2]). They take as their starting-point *o*-chlorocinnamic acid, which they prepare by heating *o*-chlorobenzalchloride with glacial acetic acid and potassium acetate on an oil-bath. The *o*-chlorocinnamic acid they reduce electrolytically into hydrochlorocinnamic acid (*o*-chlorophenyl propionic acid). This acid they heat with soda liquor in an autoclave, when melilotic acid is formed, which in turn is converted into its anhydride by boiling. The best method of obtaining coumarin from melilotic anhydride is by heating the anhydride to between 270 and 300° and slowly passing bromine over it. By this method pure, non-brominated coumarin is obtained, in addition to about 20 p.c. of resin. Chlorine also in this case acts as a dehydrating agent, and the yield of coumarin likewise amounts to from 70 to 80 p.c. Coumarin is also obtainable by simply boiling

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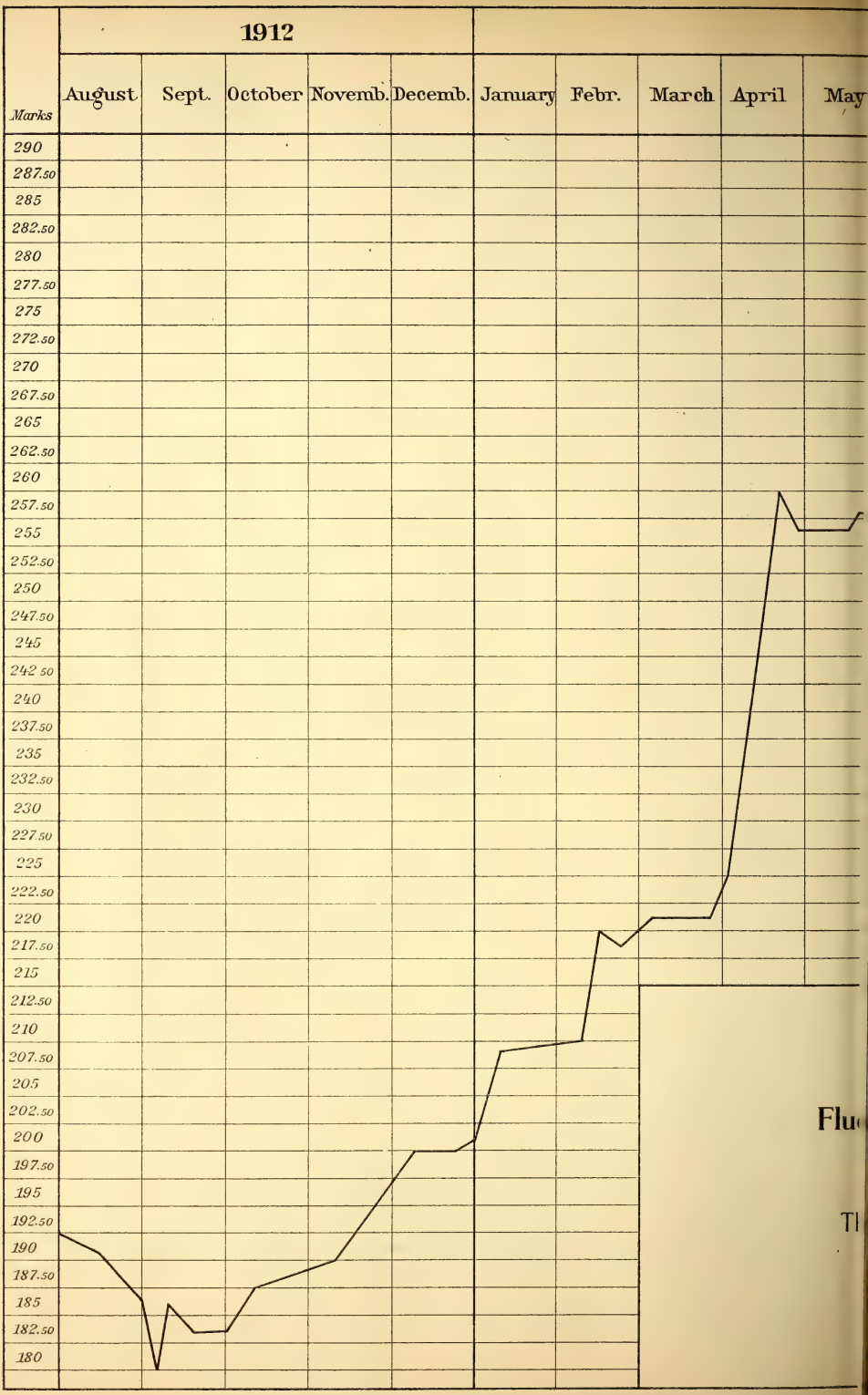
[1]) *Bulletin van het Koloniaal museum te Haarlem* No. 52, p. 101, Amsterdam 1913. — [2]) *Monatsh. f. Chem.* 34 (1913), 1665.


1912
Marks
August
Sept.
October
Novemb.
Decemb.
January
Febr.
March
April
May
290
287.50
285
282.50
280
277.50
275
272.50
270
267.50
265
262.50
260
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252.50
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187.50
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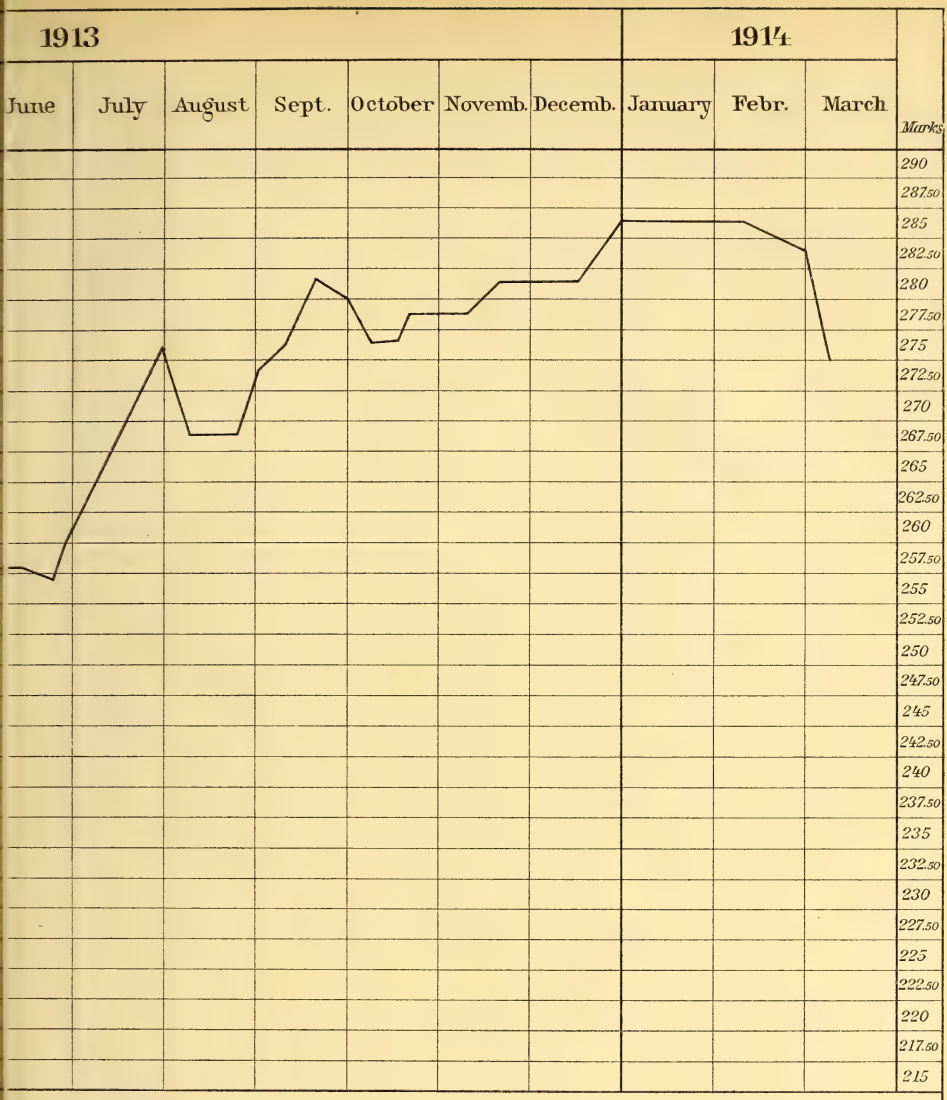
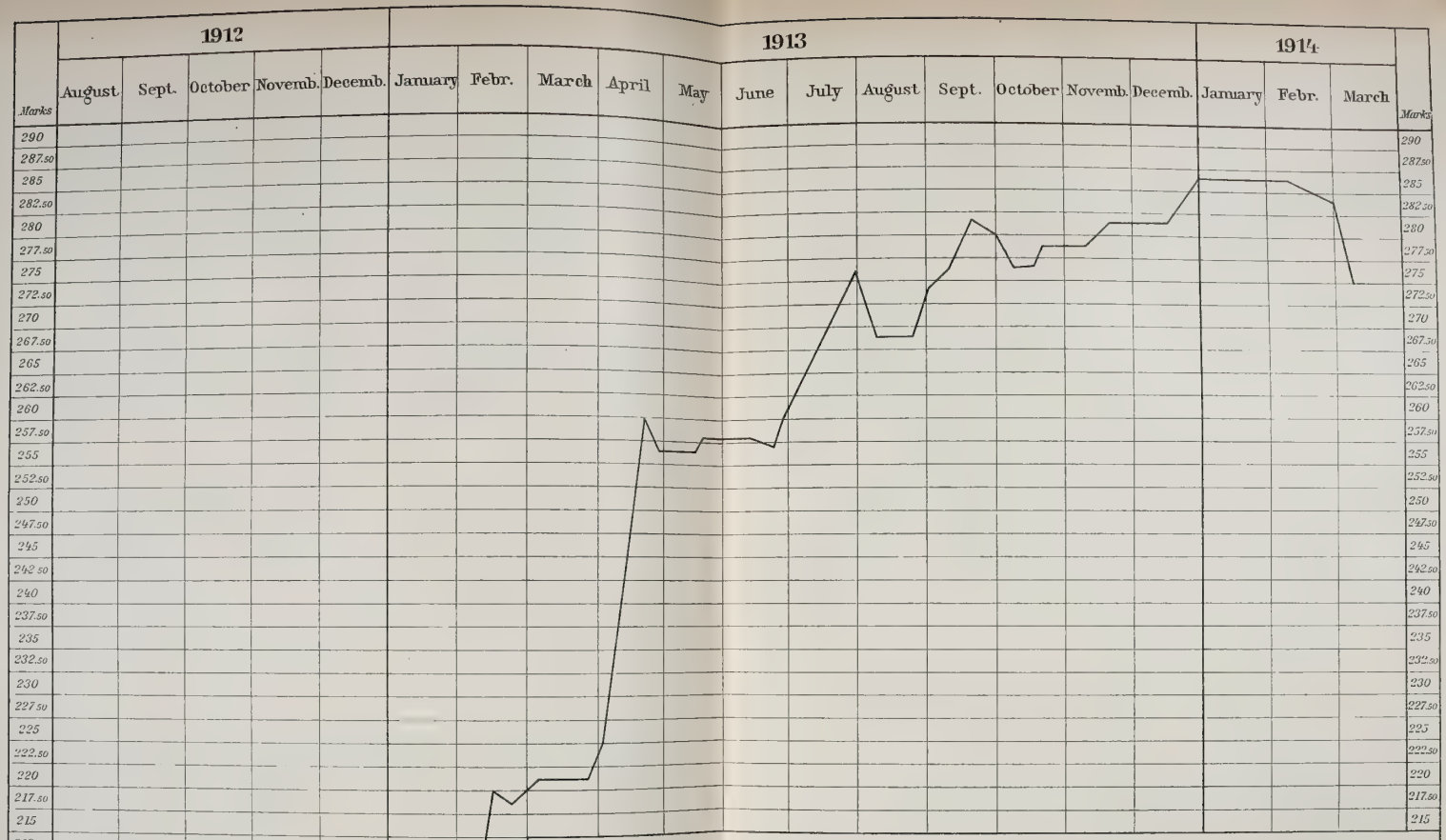
180



ations in the prices of Sicilian sweet almonds, crops of 1912 and 1913.

rices are for 100 kilos, gross weight, c. & f. Hamburg.



Fluctuations in the prices of Sicilian sweet almonds, crops of 1912 and 1913.

The prices are for 100 kilos, gross weight, c. & f. Hamburg.

the melilotic anhydride in an oxygen-current, but owing to the liberal formation of resin the yield in this case in only about 50 p.c. Finally, the melilotic anhydride was warmed with pure sulphur, when the hydrogen was driven off in the form of sulphuretted hydrogen and a yield of fully 70 p.c. of coumarin was secured.

Eucalyptol. In view of the fact that the market for eucalyptus oils containing eucalyptol has tended steadily upwards, the unavoidable rise in the price of eucalyptol cannot have come as a surprise. At the current value of the raw material our present quotation only leaves us a very moderate profit.

Linalyl Acetate. We have recently, in these *Reports*[1]), referred more than once to inferior samples of linalyl acetate. In the course of last year we have again repeatedly met with products of this description; in fact the market appears to be flooded with them. Almost without exception the samples of linalyl acetate which have been submitted to us for our opinion have left much to be desired. As in the case of the preparations previously described, all the inferior samples revealed the presence of foreign esters (geranyl acetate, neryl acetate, terpinyl acetate), and in some cases also of terpenes, that is to say of compounds all of which may appear in the form of by-products where the manufacture of linalyl acetate is conducted in an unworkmanlike manner. We should therefore be merely repeating ourselves by again quoting particular examples. A reference to the prevailing conditions may suffice to induce caution in the buying of linalyl acetate. Many manufacturers appear to be themselves unaware of the inferiority of their wares, as must be assumed from the fact that they are most astonished when, supported by analytical proofs, the pronounced impurity of their product is made clear to them beyond doubt. In some cases the correspondence which ensued as a result of our opinion showed that the manufacturer was quite incapable of properly judging the quality of his own linalyl acetate.

Menthol. As usual, this important article is referred to under the heading "Peppermint Oil, Japanese", for which see p. 78 of the present *Report*.

In our last *Report* (p. 85), we showed in detail that the German Pharmacopœia (5th Ed.) has set up an untenable demand by requiring menthol to possess a m. p. of 44°. We found that the m. p. of menthol of good quality, when tested exactly in accordance with the prescription of the Pharmacopœia, varied from 43 to 43,5°, and we therefore take the view that slight deviations from the standard set forth above ought not to constitute a cause for rejecting the article. According to the results observed by us up to the present a deviation of 1° should be regarded as admissible, but according to the results obtained by M. Lehmann[2]) such a range does not appear to be sufficient, seeing that Lehmann found samples of menthol which were above reproach in other respects to have a m. p. between 42 and 43°. In our previous contribution to the discussion of the question we stated that we regarded a m. p. of 42° as too low, and in doing so we based ourselves entirely upon the results of our own experiences, which have been confirmed again and again so far. This fact of course does not exclude the possibility that another investigator, testing the same preparation as ourselves, may determine its m. p. somewhat lower than we have done, and it would be proper for the Pharmacopœia to take account of such a possibility and to allow

[1]) *Report* October **1912**, 122; April **1913**, 116. — [2]) *Chem. Ztg.* **37** (1913), 1447.

a margin of 2°. The m. p. of official menthol should therefore be required to be from 42 to 44°.

We entirely disagree with Lehmann when he regards such deviations, insignificant in themselves, as an adequate ground for declaring that the determination of the m. p. is valueless as a factor in the valuation of menthol, and when he proposes to substitute the solidifying point for the m. p. Apart altogether from the fact that it is decidedly simpler to estimate the m. p. than the sol. p. of menthol, the introduction of the last-named as a test would not put an end to disagreements. We therefore fail to see any advantage in the substitution of the sol. p. for the m. p. of menthol. We would rather advocate the substitution in the Pharmacopœia of the m. p. (50 to 51°) for the sol. p. in the case of thymol also, for here the conditions are similar to those which obtain for menthol, while moreover absolute solidification of thymol is not even reached in the course of the test. If the prescriptions laid down in the German Pharmacopœia, 5th Ed., in respect of apparatus and of method of estimation are observed, material differences are impossible.

The solidifying point is a factor of very different importance in the valuation of liquid preparations such as anethol and eucalyptol, where the whole mass solidifies rapidly and where a sharp determination is therefore possible. In such cases the sol. p. is certainly to be preferred to the m. p., especially because it is at the same much more easily determined. This applies in an even higher degree to oils containing anethol, and Lehmann is quite correct in laying stress upon the fact that it would have been better if the German Pharmacopœia, 5th Ed., had prescribed a definite solidifying point for fennel oil, in the place of its indefinite indications as to the behaviour of the oil during cooling and subsequent warming. We, however, regard Lehmann's proposed sol. p. of 2 to 3° for fennel oil as too low, for a sample of good oil of Pharmacopœia quality should not solidify below +5° (after being cooled to +3°). We have already put forth this demand on a previous occasion[1]), when discussing the essential oils of the German Pharmacopœia, 5th Edition.

Musk, Tonquin. The exports of musk from Shanghai in the year 1913, as compared with preceding years, are set forth in the table below: —

Year	Paris	London	New York	Germany and Austria	Total
	Catties	Catties	Catties	Catties	Catties
1913	260	127	308	15	**710**
			compared with		
1912	320	183	287	36	**826**
1911	417	155	317	20	**909**
1910	722	239	287	65	**1313**
1909	480	161	186	60	**887**
1908	666	37	211	9	**923**

With regard to the smallness of the shipments to Germany, it should be stated that a considerable part of the German consumption is included in the figures referring to Paris, that city having become the leading European centre of the musk-trade. In spite of the paucity of the total shipments as compared with those of previous

[1]) *Report* April **1911**, 128.

years, the stocks in Shanghai are but small, and as the supplies from the interior of China have also diminished, the prices of genuine musk will in all probability be maintained at their present level at the very least. Attention may be called to the fact that we always hold a large stock of first-class quality, exvesicated by ourselves.

Neoviolone, Schimmel & Co. In harmony with the declining price of the raw material, we have been able to reduce the price of our ionone-preparation on several occasions. Our 100 p.c. neoviolone is an exquisite violet-perfume, which is appreciated by all consumers who attach special value to the greatest possible purity in the basic material of their violet-scents. We shall be very pleased to meet buyers of important quantities by granting them specially favourable terms.

Novoviol, Schimmel & Co. This article is steadily acquiring greater popularity in the manufacture of violet-soaps. In regard to the price, the statement made under "Neoviolone" also applies here.

Ngai-Camphor. There are two centres of production of Ngai-camphor[1]), namely the Island of Hainan and Southern China. From Hainan about 15000 lbs. of Ngai-camphor is shipped to Canton every year, where it is purified, and from where about 10000 lbs. is exported yearly. In the South of China about 15000 to 18000 lbs. of the camphor is produced yearly, and is consumed locally.

It is possible that the production of the Chittagong District in Burma may become of importance, for in that locality the *Blumea* grows in profusion. It is said that at least two species are reputed to yield Ngai-camphor, but unfortunately these are not particularised.

We reported in detail on the constitution of Ngai-camphor some time ago[2]).

Peru Balsam. Generally speaking, prices have remained unchanged, but owing to the unsatisfactory demand the tendency of the market is weak. The article still continues to suffer from the unedifying practices on the prevalence of which we have so often commented in the past that it is unnecessary to repeat our statements here. Any merchant who, like ourselves, will on principle only deal in pure Peru balsam, can derive but little satisfaction from the trade, seeing that it is an open secret that by far the great majority of the commercial balsams which pass the Pharmacopœia-tests, are in reality artificial concoctions.

K. Dieterich[3]), in a paper on artificial and genuine Peru balsam, dealt with the question to what extent the methods for differentiating and identifying genuine from artificial Peru balsam which are at present known, but are not incorporated in the 5th Edition of the German Pharmacopœia, can be used in conjunction with each other, and which of them can be utilised for the detection of artificial balsam in the natural product. He also discussed whether the methods of testing laid down in that Pharmacopœia were specially adapted to the elucidation of this problem and what proposals should be recommended for adoption in a new Edition of the Pharmacopœia.

With the object of settling the last-mentioned question, all known methods, qualitative and quantitative, were thoroughly tested, both with a series of genuine

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[1]) *Journ. d'Agriculture tropicale* **13** (1913), 317. — [2]) Comp. *Report* April **1910**, 148. — [3]) *Berichte d. deutsch. pharm. Ges.* **23** (1913), 622.

balsams and with artificial products. The result of the experiments, which are not yet quite completed, may be summarised as follows: The estimations of specific gravity, acid value, saponification value, iodine value, cinnameine-content, saponification and iodine-values of the cinnameine, resin-esters and constituents insoluble in ether, each taken by themselves, are incapable of establishing a differentiation of artificial from genuine balsam, let alone the detection of an adulteration with artificial balsams. But when all the methods of testing are carried out successively, and, when the values thus obtained are compared with the corresponding values of a pure sample, it is quite possible to identify the genuine balsam on the one hand, and the artificial product on the other, as such. It is also possible in this way to detect the presence of considerable proportions of an artificial balsam in a genuine balsam, because in every case some determination or another gives an abnormal value. It is absolutely indispensable however, in such cases, always to have at one's disposal a really genuine sample for purposes of comparison. Owing to the diversity of the artificial products it is also, of course, necessary not to be satisfied with quantitative methods, but to amplify them by qualtitative tests, for only by these combined methods is it possible to detect adulteration of the grosser kind, especially because no absolute but only relative requirements can be set up in testing. For there can be no doubt that even those imported balsams which have been pronounced genuine have been more or less sophisticated in the country of origin, and care should be taken that they remain in the condition in which they were imported, and are not still further adulterated in the country of destination. Hence those values and reactions should be used as a basis which experience has shown to apply to a product purchased from reliable commercial firms.

Of the numerous qualitative tests only a few are of use. First among these Hager's light petroleum test as modified by Enz should be mentioned: when 5 drops of genuine balsam are shaken up with about 8 cc. of cold light petroleum (temp. below 12° C.), a resinous separation ensues, which immediately adheres firmly to the side of the test-tube. The light petroleum remains quite clear and no flocks or sandy or powdery constituents are separated out from it. It is important that light petroleum of a low density (0,650 to 0,660), should be used for the test. Another suitable test is that with nitric acid, applied by the method proposed by Fromme[1]): 2 grams of balsam are vigorously shaken in a medicine-bottle with 10 grams of light petroleum; the light petroleum is then filtered off into a dry porcelain dish which has previously been most carefully cleaned, first with sulphuric acid and afterwards with water; evaporated on a steam-bath, and the residual cinnameine again heated for 10 minutes more on the steam-bath. After cooling 5 drops of nitric acid (d 1,38) are added to it, and both liquids are mixed together quickly and thoroughly in a porcelain mortar which has also been most carefully cleaned, first with concentrated sulphuric acid and afterwards with water. Pure Peru balsam immediately gives a golden-yellow colour, artificial products take a different colour.

In addition to the above, the two following qualititative tests of the Swiss Pharmacopœia are said to deserve commendation. The first, the so-called carbon disulphide test, requires that 3 parts of Peru balsam shall give a clear solution with 1 part of carbon disulphide; when 9 parts more of carbon disulphide are added, a sticky brown resin is separated out which is soluble in dilute potash-liquor, and is again precipitated from the solution by dilute hydrochloric acid. The yellow carbon disulphide solution

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[1]) Compare *Jahresbericht von Cäsar & Loretz*, Sept. **1913**, p. 115.

poured off from the resinous separation does not fluoresce, and when the solvent has been evaporated from it, affords a yellowish-brown oil, which should develop no foreign odour when heated to 150°, and should acquire at first a transitory cherry-red and afterwards an orange-brown colour upon the addition of a mixture of equal parts of sulphuric and nitric acids.

In the other test, which Dieterich calls the light petroleum test, 1 gram Peru balsam is heated for 10 minutes with 10 cc. light petroleum on a steam-bath on a reflux-condenser. Then, when 2 cc. of the poured-off solution are evaporated, the residue should not assume a greenish or bluish-green colour when a drop of nitric acid (specific gravity 1,42) is added to it. 3 cc. of the light petroleum solution, when shaken with 3 cc. of copper acetate (1:1000) should not acquire a green or bluish-green colour.

As the outcome of his investigations, the author concludes that the present test of Peru balsam requires suitable amplification. He is of opinion that, in addition to the estimation of the acid value, the saponification value, the cinnameine-content, (for which the author demands 60 p.c. instead of the 56 p.c. prescribed by the German Pharmacopœia, 5th Ed.) and the saponification value of the cinnameine certain qualitative tests should be adopted. For the latter he believes the two Swiss Pharmacopœia tests enumerated above, together with Enz's light petroleum test and the nitric acid test to be the most suitable. In conclusion, Dieterich recommends the characteristic zone-test[1]) which he has worked out, and which is easily made with a little practice. This test consists in extracting the resin-ester, (after dissolving it in soda liquor and separating it out with hydrochloric acid), with ether, carefully underlaying the ethereal solution with sulphuric acid, and adding hydrochloric acid. In all cases there results a beautiful red coloured lower zone and, where the balsam is genuine, a red-brown upper zone. When all these tests are applied it is at any rate possible to detect the principal artificial products now known and the other usual modes of adulteration which are practised.

It should be added that Dieterich's paper was discussed in detail by Enz[2]), who in his criticism again recommends his own light petroleum test and foreshadows further contributions on the subject.

Phenyl-Ethyl Alcohol. This preparation plays a very important part in modern perfumery, and its increasing consumption warrants the belief that it has a great future. Phenyl-ethyl alcohol is a body which was first detected in rose-blossoms, but it also occurs in the oils of other flowers, such as Réunion geranium oil and neroli oil. Its principal use is in the manufacture of the newer rose-scents and in rose-soaps. The most important properties of a pure article are as follows: $d_{15°}$ 1,023 to 1,026, b.p. 220 to 222°.

Pollantin. The well-known collaborator with Prof. Dunbar in his fundamental researches into the pathology of hay-fever, Carl Prausnitz, is the author of the chapter on "Hay-fever Poison and Hay-fever Serum" in the *"Handbuch der pathogenen Mikroorganismen"*[3]). This article covers 30 pages, and it is our purpose to discuss it here at some length, especially for the benefit of that numerous section of new readers of our *Report* who are interested in the subject. The first portion of the article deals

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[1]) *Berichte d. deutsch. pharm. Ges.* **18** (1908), 142. — [2]) *Südd. Apotheker-Zeitung* **1914**, 94; *Apotheker Ztg.* **29** (1914), 168. — [3]) *Handbuch der pathogenen Mikroorganismen*, edited by Kolle-v. Wassermann. 2nd Ed., Vol. II. p. 1469. Published by Gustav Fischer, Jena. 1913.

with the symptoms peculiar to hay-fever. It is well-known that the disease only attacks subjects specially predisposed to it, and that it cannot be artificialy provoked in those who are proof against it. The symptoms of the disease consist in acute inflammation of the mucous membranes of the eyes and the nose. They manifest themselves first by itching and titillation of the mucous membranes, followed by copious discharge of liquid matter and swelling of the organs; the conjunctiva and the eyelids become œdematic; they contract and become sensitive to light; and the patient begins to suffer from exceptionally frequent attacks of sneezing, finally resulting in the stoppage of one, or both of the nasal passages. The consequent enforced mouth-breathing next leads to similar symptoms in the mucous membranes of the mouth and pharynx; attended in not a few patients, particularly in the later stages of the malady, by exceedingly painful asthmatic attacks. Side by side with all the above symptoms the patient experiences a feeling of extraordinary depression and exhaustion, lassitude, and disinclination to bodily and mental exertion. After a definite period, generally after from six to eight weeks, the trouble gradually vanishes and the tormented patient once more enjoys a respite until the following year, when the attacks set in again. Spring is invariably the period of the year when hay-fever makes its appearance, at least in our latitudes; in more Southern regions, where the plants flower earlier, it commences about the end of April or the beginning of May; in Northern Germany about the middle to the end of May, and in England, the classical hay-fever country, in the first half of June. It may here be observed that the disease is rarely accompanied by fever, and that it would therefore be more correct to call it hay-cold. In the United States the disease appears in two separate forms, differing both in point of season and of cause; one occurring in the late spring and known as "Spring cold", "Rose cold" or "June cold", while another and more severe form, appears in the late summer or early autumn, and is known as "Autumnal catarrh". There are sporadic instances of patients who are subject to both forms, and these are the victims, from June until the late autumn, of their unfortunate predisposition.

The problem of the cause of the affection has been the subject of numerous investigations in the course of the last century, since Bostock, an English physician, first described the disease carefully and scientifically in the year 1819, and the most widely-differing theories have been advanced in regard to it. Bostock ascribed the affection, of which he recognised perfectly the regular recurrence, to the first moist heat of spring, to a too powerful glare of the sun's light, or to the presence of dust or similar atmospheric influences, which, in his idea, attacked the eyes. But as these effects are not restricted to the clearly-circumscribed period of hay-cold this explanation was obviously unsatisfactory. Elliotson, in the year 1831, adopted another view of the determining cause, and looked for it in the pollen of certain plants, but apparently without having any experimental foundation for his theory. Such experimental proof was not afforded until the year 1873, when Blackley showed that certain pollens, such as those of rye and other graminaceous plants, of which the presence in the air at the hay-fever period was then established, were capable of provoking the typical symptoms when brought into contact with the mucous membranes of predisposed subjects; and that it was also possible to set up similar symptoms by rubbing the pollen upon the previously scarified skin of the patient. Under the influence of the rise of the science of bacteriology, which began to develop soon afterwards, this pollen-theory, which has now again been recognised as the correct one, was abandoned in favour of one first propounded by von Helmholtz, which ascribed the cause of hay-fever to the action of bacteria. Helmholtz and other investigators discovered in the secretions

of the pituitary membrane of patients, vibrionidæ and staphylococci, and these were proclaimed by their discoverers as the cause of hay-fever, although apparently this theory was not put to the test experimentally by infecting sensitive mucous membranes with bacteria-cultures. Other authors, again, traced the origin of the disease to certain odoriferous substances or other volatile emanations exhaled by plants at flowering-time.

The researches of Dunbar, in collaboration with Prausnitz, Kammann, Weichardt, Kattein, Liefmann, Lübbert, and others, which were commenced about the year 1902, have completely cleared up these mutually contradictory and partly unverified theories. It is impossible in this place to enter at length into an exposition of the many painstaking separate investigations of the above-named and other enquirers in this sphere of research; for such particulars we must refer to our previous *Reports,* but we may summarise below the outcome of their research in three general rules laid down by Prausnitz: —

1. The pollens of graminaceous plants only set up the symptoms of hay-fever in subjects predisposed to the disease; not in normal subjects.
2. During the hay-fever season the pollens of graminaceous plants are present in the atmosphere in sufficient proportions to set up attacks of hay-fever.
3. The variations in the proportion of pollen of graminaceous plants present in the atmosphere, generally go parallel with the degree of virulence of the attacks of hay-fever.

The question in what manner the pollens which cause hay-fever act upon sensitive mucous membranes led to further thoroughgoing investigations. The exterior form of the pollens differs greatly; those of graminaceous plants are smooth and round or oval-shaped, those of the *Ambrosia*- and *Solidago*-species, which in America provoke the autumnal catarrh described above, have round or pointed protuberances. It was therefore impossible to connect the exterior shape of the pollens with their property of provoking hay-fever, and, the theory of mechanical causation being thus overthrown, there only remained the possibility of chemical processes as the determining cause of the pathological irritation. These conditions were thoroughly explored by Kammann with the pollen of rye. A chemical investigation of the constitution of this pollen gave the following results: water 10,2 p. c., ash 3,4 p. c., organic substances 86,4 p. c. Of the last-named, 3 p. c. were waxy or fatty bodies soluble in alcohol and ether, 25 p. c. hydrocarbons (starch), 18 p. c. nitrogenous bodies of a non-albuminous character, and 40 p. c. albuminous bodies. The pollen was ground to an impalpable powder in a mortar and extracted with a 5 p. c. solution of common salt for from 5 to 10 hours at a temperature of 37°, with the addition of 0,5 p. c. of phenol. The empty bags of the pollen and the rods of starch remained undissolved by this treatment. It may be that these were the bodies which earlier investigators mistook for vibrionidæ. When thoroughly washed out and tested on hay-fever patients, they proved to be inert, as also did the pollen-extract which was soluble in ether and alcohol; the untenable character of the theories of the activity of "vibrionidæ" and odiferous substances being thus clearly established. On the other hand it was found that the solution, when separated from the undissolved portions by centrifugal action, had a pronounced effect upon sensitive mucous membranes. The albuminous bodies were now precipitated by adding a large excess of alcohol to the clear toxic solution, and these bodies were found to exhibit the irritant properties of the pollen in an increased degree. By re-dissolution and fractionated precipitation by means of the familiar salts employed in separating albumins (ammonium and magnesium sulphates), it was further shown that the body which sets up hay-fever is attached to the albumin-fraction of the crude

albumen, that is to say, that it occurs in the readily-soluble portions. The aqueous pollen-extracts had no keeping properties, but the solid crude-toxin prepared by precipitation by alcohol was found to be specially suitable for clinical experiments and other investigations, because it could be kept for years without undergoing change. The average minimum limit of activity of the toxin was found to be 1 to 2 drops of a 1 : 40 000 aqueous solution. According to the calculations of the weight of pollen made by Kammann this infinitisimal quantity equals from 2 to 4 individual pollens, yet it is quite sufficient to provoke within the space of a few minutes the objective and subjective symptoms of hay-cold in patients of normal receptivity to toxic influences. This calculation agrees with Liefmann's estimates of the proportions of pollen present in the atmosphere during the hay-fever season. More sensitive subjects responded to still weaker dilutions of the toxin-solution. The symptoms, which of course are capable of being provoked at any time of the year, corresponded in every respect with those of genuine hay-fever. But Prausnitz, experimenting on himself, was able to provoke more or less pronounced symptoms of the disease not only by contact of the toxin with the mucous membranes, but also by subcutaneous injections and even by a mere rubbing of the solution on the sound skin. In his case, the symptoms following subcutaneous injection were particularly strong; they manifested themselves by a swelling of the arm to twice its normal size at the point of injection and by urticarious exanthema over the whole body. On the other hand, a medical man who was not predisposed to hay-fever, when subjected to the same treatment, remained practically free from any symptoms.

The discovery of the cause of hay-fever had important consequences upon the treatment of the disease. New methods of treatment, directly attacking the cause, superseded the purely empirical remedies, such as the excessive administration of narcotics, including cocaine, and adrenalin, which contracts the cells and impedes secretion. The form of treatment nearest at hand was the negative, prophylactic one, the patient being warned to avoid as far as could be contact with those species of pollen which were known irritants, or, where possible, to seek refuge in places where there are none or few toxic pollens, say certain high-lying mountain resorts, or islands such as Heligoland. The same object is effected by change of residence, always selecting places where the fatal plants are not yet in flower, or have flowered. Few persons, however, are in circumstances which allow them to suspend their ordinary occupations and to keep changing their place of abode for a sufficiently long period, and measures were therefore devised to afford some sort of protection against the pollen in the patient's ordinary environment. It was attempted to achieve this object by the use of glasses of the nature of motor-goggles, affording protection from the penetration of dust, and, for the nose, by cotton-wool plugs in small frames, worn inside the nostrils. With the object of rendering more difficult the solution of pollen which might penetrate in spite of these precautions, patients were recommended to rub slightly with some fatty substance the mucous membrane of the nose before the secerning of the mucous. Another mode of treatment was soon added to the foregoing. A specific irritant of a toxic character being now known to be the cause of the trouble, the possibility was recognised of a specific biological method of treatment resembling that employed in diphtheria and other infectious diseases, that is to say, of serotherapy. Dunbar soon afterwards instituted investigations in this direction. He commenced by giving subcutaneous injections of the clear, aqueous pollen-extracts to small animals, such as rabbits and goats, and afterwards to horses, and observed that, as a rule, animals rarely react towards such injections, and that when they do, they

Gathering the Pollen of Golden Rod (*Solidago Shortii*. Torr. & Gray), for immunizing the hay-fever horses.

The zinc vessels, filled with water, contain the flowering tops of golden rod, which shed their pollen on the blue paper beneath.

do so in a much feebler degree than human beings, and in a manner different from the latter. Animals whose organisms respond to the toxin only very rarely show such symptoms as irritation of the mucous membranes; the chief symptoms in their case being local swellings at the place of injection, attended by a considerable rise in temperature and distaste for food. When these symptoms disappear within a few days, the inoculation is repeated with about $1^1/_2$ times the previous dose of toxin. By this method it was found possible in many cases of horses, after an initial dose of $^1/_2$ g. of rye-pollen, to increase the dose to extracts up to 50 g. of pollen. Gradually antagonising substances against the pollen-toxin were formed within the blood-serum of the animals, as was demonstrated for one thing by their slow habituation to the poison. Another method of proving the formation of the gradual antibodies was the fact that a drop of active toxic solution, mixed with a little of the blood-serum of animals which had undergone a prolonged course of inoculation, failed to provoke the usual irritation of the mucous membrane sensitive to hay-fever, whereas the same toxin-solution after being mixed with the normal serum of various species of animals underwent no decrease of activity. It was even possible, within certain limits, to follow quantitatively the neutralisation of the toxic action on eyes sensitive to hay-fever, and on the basis of a constant dose of the toxin-solution, to measure the degree of activity of the serum, its so-called valency, within about 10 p.c. of accuracy. This was done by incorporating into the eye of the patient one drop of a toxin-solution of 1:20 000 after mixing it with an equal drop of the serum under examination. If no symptoms of irritation were observed, the toxin was completely neutralised by the protective substances of the serum. When the serum is diluted twice, five times, *n*-times, and a mixture of the same toxin-solution and of the diluted serum is introduced into the other eye of the patient after a lapse of about 10 minutes (it is quite possible to examine both eyes alternately at intervals of 10 minutes), adegree of dilution is finally observed in which the poisonous action of the toxin is no longer suspended, but in which it finds expression in a more or less pronounced irritation. By suitably varying the degree of dilution, a point is reached where only subjective irritation, such as burning or itching, is manifested, but where no objective symptoms are observed. This point is called the limit of reaction, and the degree of dilution of the serum which, together with the toxin solution, sets up this limit of reaction, is known as the degree of activity, or more briefly the valency, of the serum. It is worthy of note that, in the author's own experience, after experiments of this character, repeated several thousand times, neither local immunity nor local hyper-sensitiveness of the conjunctiva was observed, and also that the minimum limit of the quantity of toxin which provoked any effect whatever in him was not materially increased. However simple this test by means of the ophthalmo-reaction[1]) may appear to be, it has nevertheless this drawback that it is not easy to find persons who are suitable subjects for such experiments. Attempts have therefore been made to utilise the reaction employed for differentiating other vegetable species of albumin for the estimation of the value of the protective serum. So far, however, these experiments have not been successful; neither old nor fresh pollens or their extracts have ever yet afforded such a reaction. Dunbar discovered, nevertheless, that in the case of a small number of hay-fever patients the blood-serum had a clear, albeit faint precipitating action upon pollen

[1]) The ophthalmo-reaction can be very easily applied for the diagnosis of hay-fever as distinguished from other similar affections which are not due to infection by pollen *(e. g. Coryza nervosa)* by means of our Hay-Fever Diagnostic, which is supplied free of charge and ready for use to the medical profession.

solutions, but this disappeared before the winter. It is probable that these are sporadic cases, and that in any event they are not utilisable for estimating the value of the serum. Dunbar was, however, able to prove that pollen-extract, and pollen antitoxic serum, actually react together in a specific manner; this proof being afforded by the complementary uniting-test. This symptom was also observed in the blood of a few patients, and it also disappeared again before the winter.

Chemical examination of the antitoxic serum[1]) by Dunbar, Prausnitz and Kammann resulted first of all in the discovery that the protective substances of the serum are combined with the fraction of the euglobulin of serum albumen. These bodies are very susceptible to heat, a previously neutral mixture of toxin-solution and antitoxic serum, when warmed for half an hour to 75°, again exhibiting irritant powers, although in a less pronounced degree than those of the toxin-solution alone. The observation that increasing quantities of rye-pollen toxin solution do not require equally rising quantities of serum in order to prevent irritant action, but much larger quantities, was particularly striking, because it did not agree with previous experience. This fact, however, was observed both by Dunbar and by Prausnitz. It is true, however, that Kammann had previously found that in cases of acquired sensitiveness to ambrosia pollen toxin equal quantities of the toxic substance were neutralised by equal quantities of serum, this fact being in agreement with the law of multiple proportions which applies to genuine toxins[2]). Prausnitz first recognised that the cause of this abnormal behaviour of rye-pollen toxin and its antitoxin was the smaller avidity of the haptines of horse-serum for the toxin as compared with the avidity of the receptors of the patient's serum; part of the toxin remains dissociated in the mixture and requires for its neutralisation fresh supplies of serum. Other investigators drew from this abnormal behaviour the conclusion that the poison of rye-pollen was not a true toxin but an endotoxin, and the antitoxic serum no antitoxin but a cytolytic amboceptor. If this theory were correct, the bringing-together of the two substances in question with the complement body of the serum must be attended by dissolution of the pollen-cells, that is to say, in lieu of a neutralisation of the toxin the reverse must take place, namely an increase of toxic action. But Prausnitz showed that this supposed increase in solubility of the pollen under the influence of antitoxic serum is not founded on fact; the pollen is not more soluble in antitoxic serum than in normal serum, inactive serum, or other human or animal body-fluids. In opposition to this view, the opinion was put forward that it was not the pollen-cells, but the albumin of the pollen-substance which was dissolved by the serum and built down to a poison by chemical processes; and that the pollen-cells were of themselves non-poisonous, but were split up into toxic substances by the aid of the antibody and of the complement which is to be found in every normal serum. This theory involves the existence of a parallel between hay-fever and the condition of hyper-sensitiveness known as anaphylaxy; and as a matter of fact, hay-fever has in many quarters been directly described as an anaphylactic symptom, a view which, in Prausnitz' opinion, is supported by many arguments well worthy of attention, which he discusses seriatim. On the other hand, Prausnitz does not disguise from himself that other facts may be explained as opposed to the anaphylactic theory of hay-fever, and in the end he concludes that the experiments which have been undertaken so far make it impossible at present to decide whether hay-fever is a disease of intoxication or an anaphylactic manifestation. Prausnitz sums up the

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[1]) This is our Pollantin, which is available in the form of powder, liquid serum, or ointment. — [2]) See abstract on p. 117.

state of our present knowledge of the character of hay-cold in the following hypothesis: Apparently, predisposition to hay-fever has its cause in the presence of relatively small quantities of an amboceptor which is specific for pollen-albumin. Under the influence of this amboceptor the pollen-albumin which comes into contact with the mucous membrane is first decomposed by the complement into a poisonous by-product, from which, as the decomposing action proceeds, non-poisonous substances are formed. Given a sufficient excess of amboceptor, in other words, in the case of successful administration of serum, this decomposition-process is completed so rapidly that the poisonous intermediate product is incapable of exerting its effect. At the end of this part of his treatise, Prausnitz contradicts Weichardt's conception of the antiferment-like, arresting action of specific bodies, which according to him (Weichardt) are present in normal serum, and which, it is claimed, prevent the cytolysin of antitoxic serum of which he assumes the existence from developing its powers. Weichardt uses this theory to explain the protective action of the antitoxic serum, the existence of which he, too, confirms; but this protective action, it is said, can be set up just as readily, if not more so, when normal serum is used which has been prepared after feeding animals on flowering grass. In view of the secrecy which has thus far been observed in the preparation of this article, Prausnitz is disinclined to express an opinion as to the correctness of this assumption; he has however been unable to confirm the assertion that in normal serum, prepared by the above-described method, antibodies against pollen-toxin have been formed, inasmuch as these should have been found on testing in the patient's eye. It was ascertained on several occasions that this preparation was incapable of neutralising *in vitro* the action of the pollen-toxin or of curing hay-fever.

With regard to the clinical employment of hay-fever serum, the author expresses the opinion that it must chiefly be used as a prophylactic. The remedy should be applied in one of its three existing forms as early in the morning as possible, during the period when the patient is free from attacks, and immediately after he has risen. It should also be given several times subsequently in the course of the day, always prior to the expected attack or to a prearranged sojourn in the open air or at other places where there is danger from pollen (railway-journeys are particularly feared by hay-fever patients). The author also lays particular stress upon the avoidance of air charged with pollen, by such measures as the non-admittance into the patient's rooms of plants containing dangerous pollen, such as lilies-of-the-valley, asters, etc., the closing of windows, especially at night, when all powers of resistance are diminished and the organism is more or less unprotected. When an attack has actually declared itself, its suppression or relief by means of serum is much impeded by the irritation of the mucous membrane and the presence of secreted matter. Owing to the sensitiveness of the membranes not too large a dose of serum should be given at a time; it is preferable to give smaller, but more frequent, doses. Where these instructions are carefully observed a material improvement, and not infrequently a complete cure and removal of the disease is achieved with serum in the majority of cases, even when in its initial stages the treatment appears to be a failure, — a circumstance which is usually traceable to some error or other in the application of the remedy.

On occasion the favourable course of improvement and cure of the disease by the Pollantin-treatment was disturbed by the circumstance that in isolated cases symptoms of hay-fever declared themselves, which apparently resulted in an aggravation of the malady instead of in the hoped-for relief. But in almost all cases which were found to be amenable to the treatment it could be shown that these exceptions were

cases where the serum acted generally in the sense of a hyper-sensitiveness towards specific substances of the horse-albumin, which also found expression when normal horse-serum was introduced. Such symptoms are in the habit of manifesting themselves after repeated administration of serum from the same species of animal, as for example after repeated injections of diphtheria horse-serum. They are known as serum-disease. As such symptoms also occur in normal subjects treated with normal serum, and outside the hay-fever season, it is evident that their appearance is not limited to Pollantin as such, or to hay-fever patients, but that they are of a general character. In such cases relief can be afforded by using a diluted Pollantin (Pollantin "R"), or in obstinate cases by the employment of an antitoxic serum from rabbits, goats, &c., instead of from horses, although such a serum is not at present commercially obtainable. But it must be borne in mind that if such serums are applied repeatedly it is possible for the patient to become hyper-sensitive towards them also. It is entirely within the choice of the patient what particular species of Pollantin he will use; the serum in powder-form is recommended for the nose, the liquid form for the eyes; the Pollantin-ointment serves for both these organs, especially in hyper-sensitive cases such as described above. For the asthma which declares itself in many patients in the later stages of the complaint, Prausnitz, in view of the certainty that as a result of the stoppage of the nasal passages, pollen is bound to penetrate into the mouth, recommends preventive measures of the nature mentioned above. His statement, made in a footnote, concerning the use of Pollantin-tablets for asthma which we have recently prepared at the suggestion of Dunbar, we may amplify by explaining that Prof. Dunbar has been successful, in the majority of cases, in overcoming this most troublesome symptom by the administration of such tablets[1]). The tablets are simply allowed to dissolve in the mouth.

Prausnitz quotes extracts from the publications of Dunbar and from the Heligoland Hay-Fever League relating to the percentage-proportions of patients cured and relieved, as well as to those with whom the treatment is alleged to have failed. He points out that Dunbar's statistics embrace by far the largest number of cases. He also makes particular mention of the fact that various authorities have observed the gradual annual diminution of the severity of the attacks, and that in certain cases there has been a complete disappearance of hay-fever.

In conclusion, Prausnitz deals with the method of active immunisation described by Noon and Freeman[2]), based upon the injection of gradually increasing doses of pollen-extracts. He expresses a favourable opinion of the results of this treatment so far as they have gone. The question whether in these cases a true active immunisation has been achieved or whether an anti-anaphylactic condition has been created must, however, remain in abeyance. Prausnitz thinks that the difficulty of preparing really germ-free, sterile pollen-substance, such as is absolutely essential for subcutaneous injections in human subjects, is a question of practical importance.

Kammann and Gaehtgens[3]) oppose the endotoxin-theory of hay-fever poison set forth in the passage quoted above, and accepted by Prausnitz as a result of the abnormal conditions of combination between toxin and antitoxin observed by him[4]). The two authors in question point out that at the time when Prausnitz made his

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[1]) The following figures indicate the frequency of hay-fever asthma: Of 44 patients treated in the year 1912 ten, according to their own statements, suffered from asthma, but of 37 treated in the year 1913, 13. — [2]) Comp. *Report* April **1913**, 119. — [3]) *Ztschr. f. Immunitätsf. u. exp. Ther.* **4** (1912), 647. From a reprint kindly sent to us. — [4]) Comp. *Habilitationsschrift.* Published by Gustav Fischer, Jena. 1912.

experiments, experimental technique had not reached so high a stage of refinement as it has done at the present time. In the meantime we have become acquainted with, and have learned to take into account, the influence of temperature, time, dilution and other factors upon the strength and proportionality of the combination, and we now know that the law of multiple proportions does not apply universally, but only approximately. At the suggestion of Dunbar the authors have submitted to control-tests the conditions of combination between the toxin of rye-pollen and its anti-serum, and have been able to confirm the validity of the law which has been found to exist in the case of ambrosia-toxin and its antitoxin. They took as their starting-point the new toxin of high activity prepared by a special process[1]), and tested it, together with Pollantin, on five patients in multiples of size of 1, 5, 10, 20, 40 and 80. It was found that, contrary to the assumption of Prausnitz, both these substances neutralised each other in conformity with the law above-mentioned, provided care was taken that the change of the conditions of admixture which manifests itself in the testing of the higher multiples is counteracted by the use of dry serum, and also that the mixtures are only tested after they have been left for three hours in a thermostat. The object of the last-named measure of precaution was the conversion of the initial loose physical combination into a stable chemical compound. Comparative experiments with mixtures of toxin and antitoxin which had been left standing partly for 15 minutes and partly for 3 hours at a temperature of 37°, and both of which, when tested in the eye of the patient, had been found to be neutral, showed (after the mixtures had been passed through a gelatinised Berkefeld-filter), this difference, that the 15 minute-mixture had partly recovered its toxicity, whereas the mixture which had been prepared three hours previously had remained neutral after ultra-filtration. In order to compensate for the weakening action of filtration upon the toxin, the toxin-solution had been passed through the filter prior to its admixture with the serum, so that repeated filtration had no further reducing effect upon the toxicity.

The authors draw the following conclusions from their experiments: —

The neutralisation of the hay-fever poison by the corresponding antitoxin rigidly follows the law of multiple proportions. A reversible physical combination is followed in the second phase by a firm chemical combination. The toxin of hay-fever is more stable towards heat than its corresponding antitoxin. Hence, the first-named may again be liberated from neutral mixtures by heating to 72°.

We may here call the attention of our clients, and in particular of the pharmacists among them, to the fact that we are prepared to exchange old tins of liquid Pollantin bearing control-numbers from 166 (inclusive) downwards for fresh serum, and we therefore request them to look out such numbers from their stock and return them to us. Upon receipt the new tins will be forwarded immediately. *Powdered* Pollantin, if properly stored, has unlimited keeping quality, and for that reason, as we have repeatedly stated, we cannot undertake to exchange it.

Rose Oil, artificial. This exquisite substitute for genuine rose oil has been particularly appreciated last year, because the high prices of Bulgarian oil made the employment of the last-named article impossible for many of its regular consumers. Hence, compelled by necessity, many of those who were prejudiced against the syn-

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[1]) Comp. *Report* April 1913, 118.

thetic product have learned to form a better opinion of it, and we were gratified in hearing, especially from buyers of this class, very favourable reports of the results obtained. In many quarters we were assured that the users did not intend to return to the natural oil.

Rose Schimmel & Co. (Red Rose), Rose Schimmel & Co. (Moss Rose) and Rose Schimmel & Co. (Tea Rose). We are able to report most favourably upon the practical experience of our customers with these three artificial rose-perfumes prepared from a natural basis. They have become almost indispensable adjuncts in the preparation of high-class perfumery, and they are gaining new friends almost daily. Unfortunately, the last crop of our rose-plantations at Miltitz has turned out very unsatisfactory, and we have therefore had some difficulty in procuring a sufficient supply of the natural rose-extract which constitutes the basis of these three perfume-substances. Although we had a considerable quantity left over from the season 1912, our stocks are now beginning to dwindle seriously. We regard it as our duty to call our clients' attention to this fact, and to urge them to secure their requirements for the next three months, insofar as they have not done so already. Our rose-plantations have come well through the winter, which has fortunately been a normal one, and therefore, unless later on spring-frosts should set our hopes at naught, we may expect a favourable crop in the coming season.

Safrol. Our output, which runs into hundreds of thousands of kilos, has continued to be in brisk demand, both at home and abroad, and no stocks of any importance are accumulating. The camphor-market being unchanged, there is no prospect of any alteration in the prices of safrol for some time to come.

Thymol. Unfortunately, business in thymol has relapsed into the old unhealthy conditions. Senseless price-cutting, provoked by the "noble competition" of the Hamburg manufacturers is more than ever the order of the day, and the course of prices of the raw material has ceased to be of any influence on the market. Ajowan-seed is being offered from India at rising, or at any rate at very firm prices, whereas the Hamburg makers are practically accepting any bid for thymol that is made to them. Fortunately we are not under the necessity of taking part in such unhealthy methods of doing business.

Notes on Scientific Research in the Domain of the Essential Oils.

General.

In the issue of the New Zealand *Journal of Agriculture*[1]) of July 1913, it is pointed out that in many parts of New Zealand aromatic plants such as rosemary, lavender, and especially peppermint, might be cultivated with success. In England a different opinion appears to prevail on this subject. Thus, for instance, an English periodical[2]) shows, with an estimate of the cost of production, that peppermint-growing could hardly be made to pay in New Zealand, and would probably be unprofitable during the first few years. But if lavender, rosemary, and other aromatic plants were cultivated at the same time, the prospects might perhaps be more favourable.

The first volume of the *Annali della R. Stazione Sperimentale di Agrumicoltura e Frutticoltura* (Acireale 1912) contains a few statements which are of interest for our particular branch of trade. For example, A. Parrozzani, in a detailed article, deals with the maturing of the fruits of the *agrumi*, devoting a separate chapter to the oil yield and the analysis of the oils. L. Savastano and A. Parrozzani report on natural hybrids of the fruits of the *agrumi*. Finally, A. Parrozzani discusses a new method for the analysis of mandarin oil and the physiological action of methyl anthranilate. It would lead us too far to enter into particulars of the contents of these articles, and we must therfore content ourselves with mentioning them here.

K. Irk[3]) has investigated the optical rotations of numerous oils distilled in Hungary. In the case of angelica seed oil and sage oil he discovered slight deviations from the values recorded in the literature of the subject. For the first-named he found α_D +11 to +14,62° and for the second α_D +7,82 to +25°. In the course of years we have observed similar values with oils not originating from Hungary, namely, +11 to 13°20′ for angelica seed oil and +8°20′ to +25° for sage oil.

A. Juillet[4]) reports on the changes which take place in medicinal waters, and on the means of sterilising such substances. Distilled waters are among those pharmaceutical preparations which are most liable to change; the changes to which they are subject being partly of a physical or chemical character, and partly provoked by organic bodies such as fungi or algæ.

At the beginning of the 19th Century it was believed that changes in distilled waters caused the essential oil to be converted into "mucus". Afterwards the changes were ascribed to the formation of algæ. Not until the closing years of the last century was it recognised that the waters do not only contain algæ, but also fungi and

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[1]) *The Chemist and Druggist* **83** (1913), 414. — [2]) *Ibidem* 638. — [3]) *Kisérletügyi Közlemenyek* **16** (1913), Part 5. From a reprint kindly sent to us. — [4]) *Berichte von Roure-Bertrand Fils* October **1913**, 22.

bacteria. The fungi constitute by far the greater percentage-proportion, and among them *Penicillium glaucum* occurs most frequently and most freely; next to this come the *Aspergillus*- and the *Sterigmatocystis*-species. Many of the fungi are capable, under certain conditions, of assuming the form of yeast-cells. The bacteria generally belong to one of the following genera: *Leptothrix, Micrococcus,* or *Bacillus.* The algæ are monocellular, among them the genera *Protococcus, Hœmatococcus* and *Coccochloris* are represented.

Juillet gives several methods for obviating the formation of such organisms, in other words, for sterilising the waters. He describes an apparatus for laboratory-use with which it is easy to prepare absolutely sterile waters. Germ-free products may also be obtained by filtering through a Chamberland filter. Of importance also is the keeping of the sterilised waters, and this, by following Juillet's directions, is easy accomplish. For a description of the various kinds of apparatus and stock-bottles we must refer to the original article, which contains several good illustrations of the apparatus recommended.

Juillet's investigations included distilled cherry-laurel water, orange flower water, lime-blossom water and rose water.

Bibliography.

A French translation of the second volume of the second Edition of Gildemeister's book *Die ätherischen Öle (The Volatile Oils)* has just made its appearance. The title of the book is *Les huiles essentielles, par* E. GILDEMEISTER *et* Fr. HOFFMANN (Pp. 768, price in paper covers *fcs.* 21.50; cloth *fcs.* 25.—, Paris, J. B. Baillière & Fils) and the translation, like that of the first volume, is by G. Laloue.

The 8th volume of the *Handwörterbuch der Naturwissenschaften*[1]) contains an article by E. Deussen on Perfume Bodies, and the 9th volume of the same work an article on Terpenes by A. Kötz.

We have further to refer to a report by W. Müller[2]) on progress in the domain of the Chemistry of the Terpenes and Aromatics (May 1912 to May 1913), and to an article by A. Reclaire[3]) on progress in the domain of the Volatile Oils and Aromatics.

Two new parts have appeared of the work *A critical revision of the Genus Eucalyptus,* edited by J. H. Maiden. We refer to these parts on p. 61 under the heading "Eucalyptus Oil".

Analytical Notes.

P. C. Chattopadhyay[4]) reports on a simple apparatus called *"Tailameter"* (*"Taila"* being Sanskrit for "oil"), the object of which is the rapid estimation of volatile oils in plants and spices, without recourse to ether or any similar extraction agent, such agents being scarcely employable in the tropics. The apparatus consists of a long-necked flask of which the neck is graduated in divisions of $^1/_{10}$th cc. A swan-neck is luted to the bottom of the flask on the model of the Florentine flask, and this swan-neck can be closed by means of a cock. When the cock is open the capacity of the flask, which serves merely as a receiver, is 500 cc.

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[1]) Published by Gustav Fischer, Jena. — [2]) *Fortschr. d. Chem., Phys. u. physik. Chem.* **8** (1913), 117. — [3]) *Zeitschrift f. angew. Chem.* **26** (1913), I. 617. — [4]) *Journ. Soc. chem. Industry* **32** (1913), 968. From a reprint kindly sent to us.

The distillation-water runs off through the bent neck. When the distillation is finished the cock is closed and the oil is brought up into the graduated neck by filling up the contents from the distillate. The percentage-proportion of oil of the plant or drug is readily calculable from the volume of oil read off.

A possible source of error lies in the solubility of the oil in water, but this factor may usually be disregarded; in other cases it is possible to estimate the solubility approximately once for all and to take it into account in making the calculation.

The author specially recommends his apparatus for the estimation of the oil-content of sandalwood, ajowan, cloves, &c. To which we may add that, although the apparatus may be very useful for some purposes, it is certainly unsuitable for the estimation of clove oil, because this oil is heavier than water and cannot be introduced into the neck of the flask offhand.

The observations made by W. H. Simmons[1]) on the citronellol-content of geranium oil have induced other chemists to make similar investigations. From an article on this subject which has appeared in an English periodical[2]) we take the following abstracts: In the determination of citronellol by formylation[3]) it is immaterial whether the geranium oil is first saponified or not; the formic acid, therefore, acts upon esterified geraniol equally destructively as upon free geraniol. With geranium oil of different origin, acetylation on the one hand and formylation on the other, gave the following figures for the total geraniol and the citronellol contents: —

	Total geraniol	Citronellol		Total geraniol	Citronellol
French . . .	72,7 %	39,8 %	Corsican . .	73,7 %	45,9 %
Algerian . .	74,1 %	32,9 %	Asian . . .	72,1 %	51,0 %
Bourbon . .	73,0 %	44,3 %	„ . . .	69,1 %	62,3 %

In like manner citronellol determinations were carried out with samples of rose oil, the result being as follows: —

	Total geraniol	Citronellol
Bulgarian Rose oil . . .	70,1 to 75,0 %	30,1 to 36,7 %
French „ „ . . .	65,0 %	33,1 %
Anatolian „ „ . . .	66,7 and 73,6 %	39,2 and 26,2 %
Persian „ „ . . .	38,6 %	34,5 %

The behaviour of the last-named sample is quite abnormal, and it also differs from the others in its solidification point, which was decidedly higher, *viz.* 29 to 30°[4]).

In the case of three samples of adulterated Bulgarian rose oil the citronellol content varied from 13,5 to 22,8 p. c.

It was again found that formylation does not completely destroy the geraniol, but that a small proportion of it is esterified, and that in the case of freshly-prepared citronellol especially the results obtained are often excessive, up to 119,8 p. c. being recorded in one instance[5]).

L. V. Redman, A. J. Weith and F. E. P. Brock[6]) have lately tested a method for the quantitative estimation of phenols, including thymol, proposed some time ago by J. M. Wilkie[7]). This method is based upon the same principle as that recommended

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[1]) Comp. *Report* October 1913, 63. — [2]) *Perfum. Record* 4 (1913), 328. — [3]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd Ed. Vol. I, p. 580. — [4]) The purity of this oil is probably somewhat doubtful. — [5]) *Perfum. Record* 5 (1914), 51. — [6]) *Journ. ind. eng. Chemistry* 5 (1913), 831. — [7]) *Journ. Soc. chem. Industry* 30 (1911), 398.

by Messinger and Vortmann[1]), with this exception, that sodium bicarbonate is employed in the place of soda liquor. The authors found that very accurate results were obtained by proceeding as follows: about 50 cc. of *n*-sodium bicarbonate solution is placed in a glass-stoppered bottle of $^1/_2$ litre capacity and diluted with 100 cc. water. To this is added from a burette 15 cc. of a solution containing as much of the phenol under examination as corresponds to, say, a decinormal solution. To this added $^1/_{30}$-normal iodine solution in excess, until a permanent brown colour is obtained. The excess of iodine should amount to 20 p.c. The mixture is now vigorously shaken for one minute, diluted with 50 cc. of 2-*n*-sulphuric acid, and the excess of iodine titrated back with decinormal thiosulphate solution, 5 cc. of a 20 p.c. potassium iodide solution being added. Starch is used as an indicator. The experimental temperature should be from 20 to 25°. Of the solutions, the *n*-sodium bicarbonate solution and the 2-*n*-sulphuric acid need only agree approximately.

In order that the reaction may proceed rapidly it is important to shake the mixture thoroughly after adding the iodine-solution. When this is done the iodine-compound is formed completely within one minute. With thymol it affords thymol di-iodide. In order to make sure that any iodine which may have entered into the hydroxyl-group is again liberated, care should be taken that a little hydriodic acid is always present; hence the addition of the potassium iodide solution before the excess of iodine is titrated back with thiosulphate. Titration can only be regarded as completed when the blue colouration does not return even after a lapse of 10 minutes.

Physical Notes.

E. Hildt[2]) describes a fractionating apparatus devised by E. Chenard, in which the force exerted by the ascending steam for overcoming the exterior pressure is used for effecting partial recondensation. Between the still and the condenser which communicates with the outer air, a tube is to be placed in which the heat is perfectly isolated and in which therefore no condensation caused by cooling from without can take place. Notwithstanding this, partial condensation of steam is said to occur within the tube, this condensation being determined entirely adiabatically by the exterior action of the steam alone. This proposal is open to criticism, firstly that the resistance of the intermediary piece, (which, judging from the figure accompanying the description, consists of a quite narrow, long, spirally-beat glass-tube, fitted with parts for carrying off the condensate) in respect of the steam passing through it corresponds to a diminution in pressure which increases in proportion to the narrowness of the diameter of the tube and the rate of velocity at which the distillation proceeds. In the case under review both these conditions obviously apply. The occurrence of these conditions is known. In the second place it remains doubtful whether the shape of the splash-head as shown in the illustration admits of even an approximately adiabatic action; on the contrary, it would seem that a quite considerable degree of exterior cooling (attended by so-called "wild dephlegmation") is to be expected. Thirdly, there can be no question of any real duty against the atmosphere so far as the stationary process of conducting the steam from the still to the condenser is concerned, but only so far as regards the initial fractions at the commencement of the distillation.

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[1]) *Berl. Berichte* **23** (1890), 2753. Also comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd Ed. Vol. I. p. 594. — [2]) *Bull. Soc. chim.* IV. **15** (1914), 37.

H. Teudt[1]) explains the manifestations of the sense of smell by assuming them to be caused by the oscillations of electrons within the molecules or atoms. These oscillations of the electrons, it is said, set up periodical vibrations in the ether which surrounds the aromatic bodies. These vibrations are too faint to be perceptible in ordinary circumstances, but they are able, by resonance, to intensify other proximate oscillations, provided the latter are vibrating in suitable periods. The new hypothesis therefore assumes the existence in the olfactory nerves of electric oscillations, and the variance of the periods of these oscillations within the different nerves. When a molecule of an aromatic body approaches the olfactory organ, the periodical action upon the ether caused by its intramolecular oscillations only provokes a resonance effect upon those olfactory nerves which themselves are oscillating in a harmonious period. The intensified oscillation of an olfactory nerve induced by this excitement then becomes perceptible in the form of the sense of smell, each different nerve producing a different smell. Hence, molecules with varying intramolecular oscillations produce different odours, because they set up resonances in different olfactory nerves. As, according to the theory described above, the olfactory nerves are excited by the intermediary of the ether, it is not necessary for them to be in direct touch with the odoriferous corpuscles which happen to be within the nose itself.

The author also utilises his hypotheses to explain the exertion of the olfactory nerves as well as certain other manifestations, such as the compensation of odours, but in doing so he is compelled constantly to proceed upon new assumptions. Thus, according to his view, the fact that every human being has an individual odour, is explicable only on the theory that he produces different oscillations in the molecules of the bodies secreted by him, and that these oscillations differ in some way or other from the intramolecular oscillations of the secretions of his fellow-humans, the manner of their difference being independent of their chemical constitution. From this the author deduces further that it must be possible to set up different odour-oscillations in bodies of the same chemical constitution. He does not enter into the question of correlation between odour and chemical structure.

We are disposed to regard Teudt's explanation of the manifestations of smell as somewhat fantastic. The paraphrasing of well-known facts in new and complicated conceptions does not bring us nearer to a solution of causes. Moreover, we fail to understand why there should not exist bodies which allow the odour-oscillations to pass through them, just as there are numerous bodies which allow light to pass through. Nor is it clear to us whence the energy is derived which keeps the electrons moving in a given direction.

L. Tchugaeff and A. Kirpitcheff[2]) report on the rotatory dispersion of free *l*-bornyl xanthogenic acid and of certain derivatives of *β*-pinene. The newly prepared ethereal solution of *l*-bornyl xanthogenic acid has been found to possess abnormal powers of rotatory dispersion. After some time the dispersion becomes normal, because the acid splits up, giving rise to borneol and carbon disulphide, hence the solution possesses the normal dispersive power of borneol.

The rotatory dispersion of nopinic acid is normal. The dispersive power of nopinone is much less than that of nopinol, and depends in a high degree upon the nature of the solvent. Thus, for instance, $[\alpha]_D$ of the solution of nopinone in methyl alcohol = + 38,34° (C 8,073), in chloroform + 33,99° (C 8,062), in ethyl iodide + 20,85°

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[1]) *Biol. Centralbl.* **33** (1913), 716. — [2]) *Bull. Soc. chim.* IV. **13** (1913), 793, 796.

(C 8,058), in ethyl ether + 11,51° (C 8,035), in borneol + 11,35° (C 8,015), in carbon disulphide + 8,73° (C 8,73) and in *iso*pentane + 8,12° (C 8,011), whereas nopinone as such gave α_D + 11,51°.

Elsewhere, Tchugaeff, in collaboration with W. Pastanogoff[1]), has published a paper on the abnormal rotatory dispersion of coloured compounds. As a result of experiments with esters of *l*-menthyl, *l*-bornyl and *D,l*-fenchyl xanthogenic acid, they arrive at the conclusion that the susceptibility to temperature of the rotatory dispersion constitutes an eminently-marked property of active compounds. In the case of those compounds which have been examined this property depends not only upon the absorbing (sulphuretted) atomic complex, but also upon the character of the radical of the xanthogenate-group.

In conclusion we may allude in a few words to a paper by Tchugaeff and A. Glebko[2]) on the principle of optical superposition set up by van 't Hoff.

The authors combined the ethylesters of *d*- and *l*-tartaric acid as well as of meso-tartaric acid with *l*-menthyl or *D-l*-fenchyl*iso*cyanate respectively, and ascertained to what extent the rotation of the urethanes thus obtained corresponded to the theoretical requirements. In the course of these tests the results were found to correspond, at any rate approximately, with the requirements of the principle of optical superposition.

With the object of gaining an insight into certain physical calculations of particular isomeric compounds of the sesquiterpene series, F. W. Semmler and Feldstein[3]) have prepared a number of primary substances of the terpene series, namely nopinane, β-dihydrolimonene, carane, dihydroterpinolene, and tanacetane, and have determined the values for M_D, M_α and M_β of these hydrocarbons. They took as their starting point nopinone, dihydrocarvone, carone, pulegone, and tanacetone, heated these substances in a retort with hydrazine hydrate and so obtained the hydrazones, and converted the latter by treatment with sodium ethylate in a sealed tube into the hydrocarbons. The characters of these hydrocarbons are as follow: —

	B. p.		n_D	α_D	M_D found	M_D calc.
Nopinane	149° (747 mm.)	$d^{22°}_{22°}$ 0,8611	1,46141	± 0°	—	—
β-Dihydrolimonene	168 to 169° (750 mm.)	$d^{22°}_{16°}$ 0,8217	1,45673	± 0°	45,71	45,72
Dihydroterpinolene	169 to 170° (748 mm.)	$d^{22°}_{21°}$ 0,8189	1,45823	—	46,00	45,72
Tanacetane	156 to 157° (747 mm.)	$d^{22°}_{21°}$ 0,8158	1,44121	—	44,69	44,02
Carane	49 to 50° (9 mm.)	$d^{20°}_{20°}$ 0,8381	1,45823	— 34°	44,95	44,02

As a result of these investigations, Semmler and Feldstein believe that they have proved that the increments which are observed in molecules with tricyclic rings, are not attributable to the adjacent position of a keto-group or other group, but to the tricyclic ring itself.

Pharmaco-physiological Notes.

We referred on p. 138 of our last October *Report* to the formation and properties of a series of terpene alcohol glucosides described by J. Hämäläinen. In connection with this reference we may now make mention of the biological oxidation of certain glucosides, and of the place and mood of formation of the combined glucuronic acids

[1]) *Zeitschr. f. physik. Chem.* **85** (1913), 553. — [2]) *Berl. Berichte* **46** (1913), 2752. — [3]) *Berl. Berichte* **47** (1914), 384.

in the animal organism. Hämäläinen[1]) has discovered that when the glucosides of certain terpene alcohols are injected subcutaneously, the corresponding glucuronic acids appear in the urine. The terpene alcohol could be detected neither in the blood nor in the organs, hence there had been no splitting-up of the glucosides into alcohol and sugar. On the other hand he found in the blood, in addition to the unattacked glucoside itself, the corresponding combined glucuronic acid, from which it was evident that powerful oxidation had taken place.

Through the carefully washed-out small intestine of a rabbit narcotised with ether, Ringer's solution was passed from the *Arteria mesenterica* to the portal vein, and glucose and α-santenol were injected into the intestine. After six hours irrigation the liquid which had been passed through and the contents of the intestine were tested for glucoside, when a substance was isolated which corresponded in every particular to α-santenol glucoside. It therefore appears that a glucoside formation from alcohol and sugar had in fact taken place in the wall of the intestine.

J. Isaak[2]) has succeeded, by the intravenous injection of saturated aqueous camphor solutions, in provoking the typical, toxic action of camphor upon the central nervous system in the form of clonic spasms. In animals which have been narcotised the exciting effect of camphor is observable. In animals under the influence of chloral no increase of blood-pressure can be observed, but such an increase is shown in the case of animals of which the heart has been artificially weakened by subcutaneous injections of phosphorus.

On a case of poisoning after taking Oil of Pennyroyal, p. 76.

Phyto-physiological Notes.

At the meeting of the Philadelphia College of Pharmacy on October 17th, 1913, E. Charabot[3]) gave a lecture on the formation and distributation of the odoriferous principles in plants. In this lecture he reviewed his numerous researches[4]) in the domain of phyto-physiology.

In a paper read before the 11th International Congress of Pharmacy, held at the Hague in September 1913, E. Bourquelot[5]) gave a review of his investigations in the domain of the glucosides.

As we have regularly discussed Bourquelot's publications in our *Reports,* a mention of his interesting paper may here suffice.

I. Bolin[6]) has ascertained the presence in the leaves of *Salix Caprea,* L. of three glucosidases, *viz.* salicase, amygdalase and a β-glucoside-splitting enzyme. Their presence in the same *Salix*-species, however, is subject to variation from year to year. Thus, for instance, the β-glucoside-splitting enzyme, which was observed in one year, was absent the next from the leaves of the identical tree during the corresponding period of development. The author, by an experimental control-test, has also demonstrated that salicase is an enzyme with a specific action upon salicine.

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[1]) *Skand. Arch. f. Physiol.* **30** (1913), 187, 196; *Chem. Zentralbl.* **1913**, II. 1319. — [2]) *Pflügers Arch. d. Physiol.* **153** (1913), 491; *Chem. Zentralbl.* **1913**, II. 1419. — [3]) *Americ. Journ. Pharm.* **85** (1913), 550. — [4]) Comp. *Report* April **1900**, 50; October **1901**, 57; April **1905**, 89; October **1905**, 90; April **1906**, 104; October **1906**, 106. — [5]) *Journ. de Pharm. et Chim.* VII. 8 (1913), 337. — [6]) *Zeitschr. f. physiol. Chem.* **87** (1913), 182; *Chem. Zentralbl.* **1913**, II. 1595.

According to D. Hooper[1]), the seeds of *Carica Papaya*, L. (N. O. *Caricaceæ*), when distilled with water, afford an allyl-compound.

It is said that the flowers of *Ochrocarpus siamensis*, T. Anders (N. O. *Guttiferæ*), a tree known in British India by the name of *"Tharapu"*, develop an aroma reminding of violets.

In our *Report* of April **1903** (p. 79) we made mention of a sample of wood, a native of German East-Africa, which had been sent to us by Prof. Zimmermann, the Director of the Biological-Agricultural Institute at Amani. The wood had a pronounced odour of skatol. By extracting this substance with ether we isolated and identified it (m. p. 95°; m. p. of the hydrochloride 168°). The skatol-odour was particularly pronounced in a sample of reddish-brown wood; in a sample of white wood it was much fainter.

At the time we were unable to give any information on the botanical origin of the wood. Prof. Zimmermann has now informed us, at our request, that in the meantime the parent plant of the wood has been identified as *Celtis Durandii*, Engl. (N. O. *Urticaceæ*). It is an item of special interest that the green wood as well as the bark of the tree are almost devoid of odour, and that the skatol odour only develops when the wood has reached an advanced stage of decay. At present the conditions which account for the existence of the red wood, which has the most powerful odour, are still unknown. Experiments are being conducted at Amani to ascertain the behaviour of the wood in the course of its decomposition in water, in the earth, &c.

From the powdered parts of the root of *Serucidaca longipedunculata*, Fresenius (N. O. *Polygalaceæ*), a native of Western Usambara, W. Lenz[2]) has isolated, by extracting the material with low-boiling light petroleum, a viscous, readily-crystallising mass, with a clearly-perceptible odour of wintergreen oil. The saponification-liquid, when acidulated with sulphuric acid, gave with highly-diluted ferric chloride solution the violet colour characteristic of salicylic acid.

Chemical Notes.

A. Kötz and E. Schaeffer[3]) have worked out a new methylation-method, which is based upon the reduction of hydroxymethylene compounds into methylene compounds. Generally speaking, the hydroxymethylene compounds are very difficult to reduce by means of hydrogen and platinum metals, inasmuch as they are bodies with an acid reaction, which are apt to give flocculent precipitates with colloidal platinum metal solutions. For this reason an attempt to reduce hydroxymethylene menthone with palladium chloride in the presence of a protective colloid, resulted in failure. The reaction commenced with great rapidity, but after a while the palladium was precipitated in such coarse flakes that no further reduction took place.

A better result was achieved by shaking the hydroxymethylene menthone, dissolved in methyl alcohol, with a palladium chloride solution without a protective colloid. Already in the course of the reduction of the palladium chloride an unusually rapid absorption of hydrogen set in, and before the palladium was precipitated in flakes, 1,5 grams of the substance had been for the greater part reduced. The rest of the calculated quantity of hydrogen was also gradually absorbed after the

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[1]) *Pharmaceutical Journ.* **91** (1913), 369. — [2]) *Arbeiten a. d. Pharm. Institut der Universität Berlin* **10** (1913), 177. — [3]) *Journ. f. prakt. Chem.* II. 88 (1913), 604.

precipitation of the palladium. In reducing 10 grams of the substance, the required quantity of palladium chloride was added by degrees, whenever the process of reduction grew too slow. Under this treatment, 10 grams hydroxymethylene menthone absorbed the quantity of hydrogen calculated for the two double bonds. A liberal yield of methylmenthone, boiling between 96 and 97° (13 mm.), was obtained. Hydroxymethylene camphor, when reduced by Willstätter's method (deposited palladium black) afforded a poor yield of impure methyl camphor. A liberal yield of methyl camphor was obtained by reducing the chloride of hydroxymethylene camphor. Methyl*iso*thujon results from hydroxymethylene*iso*thujone by applying Skita's inoculation method[1]). The absorption of hydrogen proceeded very slowly. The resulting methyl*iso*thujone had b. p. 229 to 230° (103 to 105° at 11 mm.). Hydroxymethylene dihydrocarvone was reduced by the same method as hydroxymethylene menthone, giving rise to methyldihydrocarvone: b. p. 226 to 227°; semicarbazone, m. p. 168°.

An article by E. Knoevenagel[2]) contains interesting observations on the action of various catalysts in acetylation. As is well known, it is not only organic compounds containing hydroxyl which are capable of being acetylated, but oxides, aldehydes, certain unsaturated and ether-like compounds, and unsaturated ketones, as well as the anhydrides of polyatomic alcohols in open- or ring-formation, also have the power of reacting with acetic anhydride.

Knoevenagel proposes to apply the general term of acetolysis to formations of acetates which take place by the resolution of organic molecules. Herein he follows Skraup, who first observed such a molecular decomposition by the action of acetic anhydride in the case of cellulose. Knoevenagel also proposes to introduce the term "acetolysis by acetic anhydride", analogous to the use of the expression "hydrolytic processes" for decomposition by the addition of water. The acetylation of the hydroxyl-compounds and the formation of acetates in the case of the other compounds mentioned, as well as the occurrence or absence of acetolytic resolution depend not only upon the temperature and the quantity of the catalyst employed, but also, in a high degree, upon the nature of the catalyst. Given an accurate knowledge of these conditions it is therefore possible, according to the nature of the experimental conditions, and concurrently with the acetylation of any hydroxyl-groups which may exist in the molecule, either to disrupt by resolution, or to leave unattacked, any oxide group (by the addition of acetic anhydride) and eventually also the molecule.

Knoevenagel has treated with acetic anhydride numerous aldehydes, ketones and oxides in the presence of various catalysts. Among others he employed the following catalysts: ferric chloride, zinc chloride, sub-chloride of tin, trichloride of phosphorus, sulphuric acid, sulphoacetic acid, ferrous sulphate, copper sulphate, zinc sulphate, ammonium sulphate, and methylamine sulphate. The author employed three different methods of estimating the action of these catalysts, as follows: —

1. By means of the rise in temperature caused by the catalysts, room-temperature being taken as the normal.
2. By means of the yield of aldehyde diacetates.
3. By means of the melting points of the crude acetates.

The action of the catalysts may be judged by the aid of tables drawn up by the author, showing the temperature, the yield and, where possible, the melting- or boiling-point of the reaction-product obtained with each separate catalyst.

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[1]) Comp. *Report* April **1913**, 134. — [2]) *Liebigs Annalen* **402** (1914), 111.

For example, the author mixed together 10 grams pure benzaldehyde, 10,6 grams acetic anhydride (1 mol. + 10 p.c.) and 0,1 gram contact-substance. The temperature was prevented from rising above 70° by cooling with cold water. After 24 hours the mixture was washed with water and soda-solution, after which the reaction-mixture generally solidified. The benzylidene diacetate obtained by this method had b. p. 154° (20 mm.); m. p. 46°. With copper sulphate and chloride of zinc an almost quantitative yield was afforded. Benzylidene diacetate can also be prepared quantitatively without excess of acetic anhydride with sulphuric acid or ferric chloride if the reaction is prepared in a freezing mixture. In that case the entire mass solidifies at room-temperature after some time. Cinnamic aldehyde afforded cinnamylidene diacetate (m. p. 85°). In this case ferric chloride and zinc sulphate were an almost complete failure. Vanillin yielded vanillin-triacetate (m.p. 90°). Anisaldehyde afforded anisylidene diacetate (m.p. 67°); piperonal (heliotropine) afforded piperonylidene diacetate (m.p. 80°). Salicylic aldehyde and acetic anhydride yielded in part the triacetate (m, p. 103°), in part the disalicylic aldehyde (m.p. 129°), partly also these two substances together.

Cineol is capable of being split up, with addition of acetic anhydride, if the reaction is carried out in the presence of suitable catalysts. In this case, terpin diacetate and terpinyl acetate result. The formation of terpinyl acetate is probably due to the belated splitting-off of acetic acid. The addition of acetic acid to the reaction-mass lowers the yield of terpinyl acetate, and when acetic acid is used by itself the reaction proceeds with formation of dicinene. Sulphuric acid and ferric chloride are specially suited for decomposing cineol. The terpinyl acetate boils at 104 to 106° (11 mm). The terpin diacetate distilled over at 145° (14 mm.).

C. Neuberg[1]), in collaboration with H. Steenbock, reports on the formation of higher alcohols from aldehydes by means of yeast. They describe the conversion of valeric aldehyde into amyl alcohol. The authors allowed carefully purified commercial valeric aldehyde (a mixture of *iso*valeric aldehyde and methylethyl acetaldehyde), to drip slowly into a mixture of cane sugar and yeast in process of fermentation. After being left standing for 4 to 6 days the alcohol-mixture was distilled off. After drying the mixture over fused sodium sulphate and copper sulphate, it was possible to isolate the amyl alcohol by means of a Heinzelmann bi-rectificator[2]), the yield being from 66,4 to 84,1 p.c. of the valeric aldehyde used in the experiment. Sugar and yeast by themselves afforded only traces of amyl alcohol. The amyl alcohol obtained from valeric aldehyde consisted, according to the composition of the crude material, of a mixture of *iso*butylcarbinol and *l*-methylethylcarbinol. When valeric aldehyde and ammonia were used, a liberal yield of amyl alcohol was also obtained. Without the addition of sugar the amyl alcohol yield amounted only to 26,1 p.c. The amyl alcohol was identified from its b. p. and from the preparation of the α-naphthylurethane. The latter melted at 64°. The maceration-juice of yeast also has the power of reducing valeric aldehyd to amyl alcohol.

K. Ohta[3]) has likewise reduced *iso*butyl alcohol as well as œnanthol (*n*-heptylic aldehyde), a body which is foreign to the organisms, to the corresponding alcohols by means of yeast. The addition of œnanthol, however, to the fermenting sugar solution, greatly impedes the fermentation process, and when the œnanthol is added carelessly, fermentation may be arrested altogether. The α-naphtyl urethane of the *n*-heptyl alcohol had m. p. 97°.

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[1]) *Biochem. Zeitschr.* **52** (1913), 494; **59** (1914), 188. From a reprint kindly sent to us. — [2]) *Chem. Zentralbl.* **1913**, I. 968. — [3]) *Biochem. Zeitschr.* **59** (1914), 183. From a reprint kindly sent to us.

Hydrocarbons.

Camphene. We mentioned on p. 133 of our *Report* of October **1913** that P. Lipp had succeeded in identifying nitrocamphene as a true nitro-body. The same author[1]) has recently studied the action of strong mineral acids upon this compound. It was already known that when the nitro-body is dissolved in concentrated sulphuric acid, and the suitably diluted sulphuric solution is boiled, tricyclenic acid results[2]). Another conversion has been observed by May[3]) when treating the body with aqueous fuming hydrobromic acid. This reaction afforded a body $C_{10}H_{15}NOBr_2$, which was reduced without difficulty to $C_{10}H_{15}N$.

In the first-named reaction the nitrogen is eliminated in the form of hydroxylamine. Hence, Lipp assumes that a hydroxamic acid is formed as an intermediary product. Nevertheless the first intermediary product which could be isolated was not a hydroxamic acid, but the neutral sulphuric ester (I) of a hydroxyhydroxamic acid, possessing the constitution $C_{10}H_{15}O_5NS$. This sulphuric ester is readily saponifiable and then affords the basic hydroxyhydroxamic acid (II), which when warmed in a sulphuric acid solution readily splits up into tricyclenic acid (IV) and hydroxylamine. The hydroxyhydroxamic acid does not belong to the camphene series, but to the camphane series, for with nitrous acid its nitrogen was split off in the form of nitrous oxide, giving rise to a hydroxy acid (III), which proved to be identical with the hydroxyapocamphane carboxylic acid described by Bredt and May[4]). Seeing that it is highly improbable that an interchange of systems should take place when nitrous acid is allowed to react upon the hydroxyhydroxamic acid, the interchange must occur at an earlier stage, when sulphuric acid is absorbed by the double bond of nitrocamphene (V). Hence the hydroxyhydroxamic acid is not camphenylhydroxamic acid, as Lipp formerly believed it to be, but a 2-hydroxyapocamphanehydroxamic acid.

The action of hydrobromic acid is altogether different from that of sulphuric acid. In this case hydrobromic acid is first absorbed, the absorption being connected with the conversion from the camphene- to the camphane-series. Next, the nitro-group is converted into the hydroxamic acid form, while at the same time one hydroxyl is replaced by bromine. The 2-bromoapocamphanehydroximic acid bromide (VI) which corresponds to the sulphuric ester mentioned above, is much more stable than the latter. The functions of the two bromine atoms differ completely. The first is readily replaced by reacting with ammonia or aniline in ethereal solution, affording 2-bromoapocamphaneamide oxime and anilide oxime. The second bromine atom is more closely combined, but can be detached by boiling bromoapocamphane amide oxime with water, when hydroxyl is substituted for it. When the bromide is treated with methylalcoholic potash both the bromine atoms are exchanged for methoxyl, giving rise to 2-methoxyapocamphane methyl hydroxamate, which is split up into tricyclenic acid and hydroxylamine by boiling it for a short time with sulphuric acid. The body $C_{10}H_{15}N$, which had already been prepared by May from bromoapocamphane hydroximic acid bromide by reducing it with zinc dust and glacial acetic acid represents the nitrile of apocamphane carboxylic acid (VII). This conclusively shows that the bromide belongs to the camphane series. The reduction of a hydroximic acid halogenide into the nitrile of the corresponding carboxylic acid appears to be a novel proceeding.

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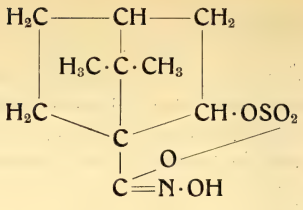
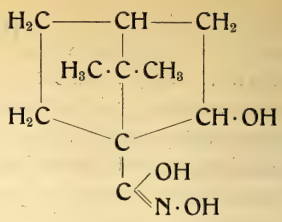
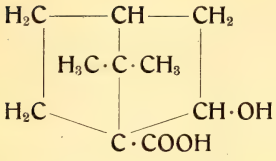
[1]) *Liebigs Annalen* **402** (1914), 343. — [2]) Bredt and May. *Chem. Ztg.* **33** (1909), 1265; *Report* April **1910**, 179. — [3]) *Dissertation.* Aix-la-Chapelle 1910, p. 65. — [4]) *Chem. Ztg.* **34** (1910), 65; *Report* April **1910**, 180.



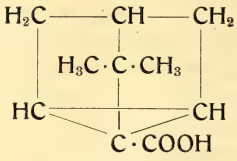
(I) Sulphuric ester of 2-hydroxyapocamphane hydroxamic acid.



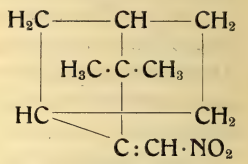
(II) 2-Hydroxyapocamphane hydroxamic acid.



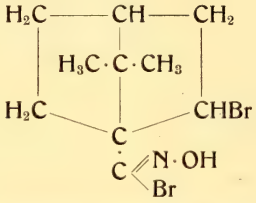
(III) 2-Hydroxyapocamphane carboxylic acid.



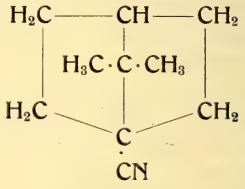
(IV) Tricyclenic acid.



(V) Nitrocamphene.



(VI) 2-Bromoapocamphane hydroximic acid bromide.



(VII) Nitrile of the apocamphane carboxylic acid.

Bornylene. In continuation of previous investigations[1]), G. G. Henderson and W. Caw[2]) have oxidised bornylene with hydrogen peroxide in an acetic solution, the bornylene having previously been purified by the method described by Henderson and Caw[3]). The most favourable temperature for carrying out the oxidation-method is from 55 to 60°, acid and neutral products, with a trace of an aldehyde, being formed. The first-named two bodies consisted of two acids, volatilising with steam: camphenanic acid (m. p. 95°) and *iso*camphenanic acid (m. p. 74°), as well as of a non-volatile hydroxy acid $C_8H_{12}(OH)CO_2H$, which did not crystallise and which decomposed when distilled *in vacuo*, giving rise to an unsaturated acid, melting at 80°. The neutral oxidation-products consisted of a mixture of esters, of which those which volatilised with steam, when saponified, yielded in addition to acetic acid, the three acids mentioned above, as well as two isomeric alcohols $C_{10}H_{17}OH$. As was to be expected, the alcohol-mixture consisted principally of borneol. The second alcohol was identified as epiborneol by oxidising it into epicamphor[4]). The esters which did not volatilise with steam, when saponified, afforded the same acids as well as two isomeric saturated alcohols $C_{10}H_{18}O_2$, respectively melting at 247 to 248° and at 235 to 236°; these latter were separated out from benzene by fractional crystallisation. So far nothing definite has been ascertained concerning the structure of these alcohols. The alcohol with

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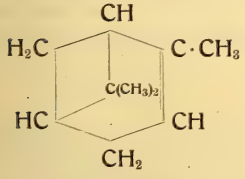
[1]) Comp. *Report* October **1911**, 134; April **1912**, 169; April **1913**, 135. — [2]) *Journ. chem. Soc.* **103** (1913), 1543. — [3]) Comp. *Report* October **1912**, 147. — [4]) See p. 140.

m. p. 247 to 248° forms a *p*-nitrobenzoate, m. p. 44 to 45°, the one with m. p. 235 to 236° yields a *p*-nitrobenzoate with m. p. 82 to 83.

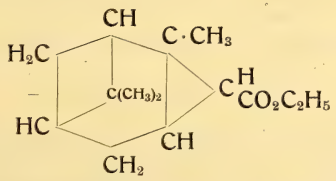
The observation that when bornylene is oxidised camphenanic and *iso*camphenanic acids are formed is of importance. These acids having been obtained both by Henderson and Sutherland and by Aschan[1]) as decomposition-products of camphene, it follows that camphene and bornylene are more closely related than had hitherto been assumed.

C. Harries and R. Haarmann[2]) report on bornylene ozonide. They treated bornylene which had been purified by Tchugaeff's method[3]), in a hexane solution with washed (8 p. c.) ozone, and obtained a white ozonide in the form of a precipitate. This ozonide was volatile and non-explosive, and decomposed very slightly when boiled with water. In order to carry out the resolution of the ozonide, the authors ozonised bornylene in glacial acetic acid instead of in hexane, and then heated the solution on a water-bath. By this method they obtained as principal product a pale yellow oil, b. p. 105 to 125° (18 mm.) and a solid substance, b. p. 125 to 150° (18 mm.). The liquid fraction contained a dialdehyd, whereas the solid portion probably contained an aldehydo-acid.

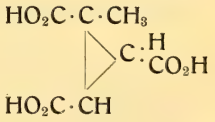
α-Pinene. On pp. 131 and 134 of our last October *Report* we referred to the interesting investigations by E. Buchner and W. Weigand on the action of diazoacetic ester upon bornylene and camphene. More recently, Buchner, in conjunction with K. Rehorst[4]), has also treated α-pinene (I) with diazoacetic ester and has obtained such products as were to be expected from the presence in the pinene-molecule of an endocyclic double bond[5]). The authors used an inactive α-pinene, regenerated from the nitrosochloride by boiling with aniline and as a reaction-product they obtained 1,6,6-trimethyl*cyclo*-(0,1,$4^{5,7}$,1)-octane-2-carboxylate[6]), $C_{11}H_{17}\cdot CO_2C_2H_5$ (II). The free acid melts at 165°. Resolution of the acid with aqueous potassium permanganate solution in the presence of sulphuric acid afforded methyl*cyclo*propane-1,2,3-tricarboxylic acid (III), m. p. 192. The m. p. of the trimethylester of this acid (76,5°) suffers no depression after the admixture of synthetic ester[7]). In the course of this reaction they obtained as by-products terebinic acid and an acid $C_{12}H_{16}O_4$ the latter arising apparently from the condensation-product by the oxidation of the methyl-group in the 1-position towards a carboxyl-group. In the course of treating non-regenerated, optically active pinene with diazoacetic ester, an acid $C_{12}H_{18}O_2$ had been formed as a by-product; this acid is presumably derived from the semicyclic β-pinene and represents a spirane-derivative.



(I) α-Pinene.



(II) Trimethyltri*cyclo*octane-2-carboxylate.



(III) Methyl*cyclo*propane-1,2,3-tricarboxylic acid.

[1]) Comp. *Report* October **1911**, 134; April **1912**, 169. — [2]) *Berl. Berichte* **46** (1913), 2595. — [3]) Comp. *Report* October **1912**, 146, 147. — [4]) *Berl. Berichte* **46** (1913), 2680. — [5]) Before this A. Loose [*Journ. f. prakt. Chem.* II. **79** (1909), 505] had already reacted upon pinene with diazoacetic ester, but had been unable to isolate any cristalline products. — [6]) This compound is named according to A. von Bæyer's method. Comp. our last *Report*, p. 135. — [7]) Comp. Buchner and H. Dessauer, *Berl. Berichte* **27** (1894), 878.

Sylvestrene. On p. 179 of our *Report* of October **1910**, we described a synthesis of *d*-sylvestrene carried out by H. W. Perkin. The same author, in conjunction with W. N. Haworth[1]), has recently also been successful in synthethising *l*-sylvestrene.

The authors took as their starting-point *cyclo*hexanone-3-carboxylic acid, which by treating with magnesium methyl iodide they converted into 1-methyl*cyclo*hexane-1-ol-3-carboxylic acid. By acting upon the last named body with hydrobromic acid they obtained 1-bromo-1-methyl*cyclo*hexane-3-carboxylic acid and this, when heated with pyridine, afforded a mixture of 1-methyl-Δ^1- and 1-methyl-Δ^6-*cyclo*hexene-3-carboxylic acid, hydrobromic acid being split off. With the assistance of the brucine- and *l*-menthylamine salts, *d*- and *l*-1-methyl-Δ^6-*cyclo*hexene-3-carboxylic acids were isolated from the acid mixture. The dextrorotatory modification ($\alpha_D + 108°$) was converted into the ethylester which, with magnesium methyliodide, afforded *d*-Δ^6-m-menthenol-8 (b. p. 106 to 107° at 20 mm.; $[\alpha]_D - 2{,}73°$). With concentrated hydrochloric acid this alcohol formed *d*-sylvestrene dihydrochloride (m. p. 72°; $\alpha_D + 22{,}5°$), a body which suffered no depression of m. p. when mixed with a preparation from Swedish turpentine oil. The sylvestrene which was recovered from the dihydrochloride boiled at 175 to 178°; $\alpha_D + 67{,}5°$.

The lævorotatory acid was not yet quite optically pure. It gave $\alpha_D - 98{,}6°$ and afforded *l*-Δ^6-m-menthenol-8 (b. p. 106 to 108° at 21 mm; $\alpha_D + 1°$) from which resulted *l*-sylvestrene dihydrochloride: m. p. 70 to 72°; $\alpha_D - 21{,}8°$. *l*-Sylvestrene boiled between 176 and 178°; $\alpha_D - 68{,}2°$. A mixture of equal parts of the two dihydrochlorides had m. p. 52°, which is the m. p. of carvestrene (*i*-sylvestrene)-dihydrochloride.

l-1-Methyl-Δ^1-*cyclo*hexene-3-carboxylic acid was also prepared in an approximately optically pure state ($\alpha_D - 49{,}7°$). It was readily convertible into *l*-Δ^1-m-menthenol-8 (b. p. 106 to 108° at 20 mm.; $\alpha_D - 45{,}9°$) which also afforded *l*-sylvestrene dihydrochloride (although not quite so readily as Δ^6-menthenol) from which pure *l*-sylvestrene was obtained.

On p. 50 of the present *Report* we describe the properties of a *l*-sylvestrene prepared by us.

Cadinene. At the meeting of the Moscow Society of Natural Science of 23 November/6 December 1913, N. Lepeshkin[2]) stated that cadinene recovered from the dihydrochloride by the ordinary methods is not a uniform substance, but contains, in the form of a by-product, an inactive product of isomerism, which he calls *iso*cadinene. Isomerism takes place when the dihydrochloride is heated with glacial acetic acid in a sealed tube, and in part also when cadinene is prepared from the dihydrochloride with sodium acetate in glacial acetic acid. By treating cadinene dihydrochloride with sodium ethylate[3]), however, Lepeshkin obtained a uniform cadinene.

On a sesquiterpene related to cadinene, see Oil of Copaiba Balsam, p. 48.

Alcohols.

Ethylamylcarbinol. R. H. Pickard and J. Kenyon[4]), in a paper announcing the results of their investigations into the dependence of rotation upon chemical constitution, describe among other things the synthesis of *d*-ethyl-*n*-amylcarbinol, which was discovered by us at the time in Japanese peppermint oil, and which we have also prepared synthetically[5]). Pickard and Kenyon passed the vapour of a mixture of 145 grams *n*-caproic acid and 180 grams propionic acid through a tube charged with

[1]) *Journ. chem. Soc.* **103** (1913), 2225. — [2]) *Chem. Ztg.* **38** (1914), 276. — [3]) Comp. *Report* October **1909**, 47. — [4]) *Journ. chem. Soc.* **103** (1913), 1923. — [5]) *Report* April **1912**, 102; April **1913**, 82.

thorium oxide and heated to 400°, by which method they obtained 124 grams of crude ethyl-*n*-amylketone. Reduction of the ketone in a solution of moist ether and sodium afforded 106 grams of crude ethyl-*n*-amylcarbinol, from which body in turn they obtained 197 grams of the acid phthalate. By fractional crystallisation from methyl alcohol the authors succeeded in preparing the optically pure strychnine salt of the *d*-phthalate. When regenerated from the phthalate, *d*-ethyl-*n*-amylcarbinol had b. p. 76° (16 mm.). The properties of ethyl amylcarbinol and its derivatives, as observed by Pickard and Kenyon and by ourselves are as follow: —

	d-ethyl-*n*-amylcarbinol				M. p. of the acid phthalate	B. p. of the corresp. ketone	M. P. of the semicarbazone
	B. p.		α_D	$n_{D20°}$			
Pickard and Kenyon	76° (16 mm.) 168 to 172° (753 mm.)[1]	$d^{20°}_{4°}$ 0,8247	+6,79°	1,4252	66 to 68°	165 to 166°	112°
Schimmel & Co. . .	178,5 to 179°	$d_{15°}$ 0,8276	+6,43°	1,4275	65,5 to 66°	170°	117°

Chromic esters of terpenic alcohols. H. Wienhaus[2]) has discovered that by merely shaking up dilute aqueous solutions of chromic acid with certain alcohols, chromic esters may be formed. When the alcohol has been dissolved in light petroleum, the layer of the latter at once acquires a red colour, and it is only necessary to evaporate the solvent in order to obtain the organic chromate. A better method is to treat the alcohols in a solution of carbon tetrachloride or light petroleum with an excess of dry chromic anhydride, and to pour them off from the unattacked reagent, which has become partly deliquesced as a result of the water which has been generated. It is best to evaporate the solutions in a vacuum-desiccator. Chromic acid being the agent for oxidising primary and secondary alcohols, the possibility of an ester of chromic acid being formed is restricted to tertiary alcohols. It is necessary, besides, that the remaining molecule shall be stable towards oxidising action.

Chromic esters are most difficult to saponify with alkaline liquors and baryta solution, probably because of their insolubility in water. When heated with alcoholic liquors, the alcohol is readily regenerated.

In organic chromates, chromic acid can no longer be identified by the usual test with hydrogen peroxide in ether.

The formation of a chromate may often serve to establish the tertiary character of an alcohol. If the solution of the alcohol in light petroleum, when treated with chromic acid, remains red for a long time, there is no longer any doubt of the tertiary character of the alcohol. If the colours of the solution should soon become mixed this fact would not prove anything, because not only primary and secondary, but under certain conditions tertiary alcohols also oxidise more quickly.

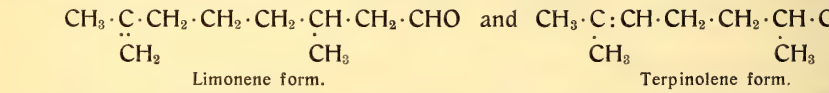
Methylfenchol, the product of reaction of fenchone and magnesium methyl iodide, gives a beautifully crystallising chromate. Contrary to methylfenchol, which is slightly dextrorotatory, the chromate is lævorotatory ($[\alpha]_{Li\,red}$ — 30,0°). It melts at 130°. The chromate of ethylfenchol is less readily soluble than that of methylfenchol. It does not melt, but turns black at 140°; $[\alpha]_{Li\,red}$ + 22,5°. The chromate of methylborneol constitutes small needles of a bright orange colour, decolorising at 105° but without melting. The chromate of cedrol forms clear, yellowish-red, narrow prisms, melting into a black liquid at 115°; $[\alpha]_{Li\,red}$ + 79,4°. Ledum camphor, or ledol, as Wienhaus

[1]) Crude product. — [2]) *Berl. Berichte* **47** (1914), 322.

calls it, affords a chromate with m. p. 92°; $[\alpha]_{Li\,red} + 30{,}0°$. From the above it is evident that cedrol and ledol are tertiary alcohols. Patchouly camphor also gives a stable chromate, but guajol does not.

We fail to find in the interesting paper of Wienhaus any reference to a compound of chromic acid and maali alcohol. It is true that the last-named body was not identified by us as a chromic ester at the time, but it is doubtless an organic chromate[1]). In the same investigation we referred to the chromic acid compounds of patchouly alcohol (m. p. 52 to 53°), of sesquiterpene alcohol (globulol)[2]) from the oil of *Eucalyptus Globulus* (m. p. 78°), and of ledum camphor.

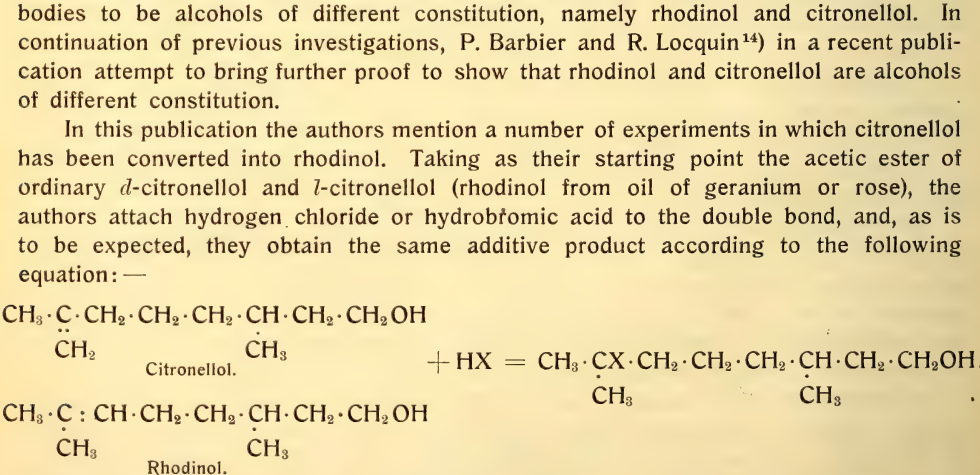
Citronellol. The investigations of Tiemann and Schmidt[3]), Semmler[4]), Harries and Himmelmann[5]) on the one side, and those of Harries and Roeder[6]) and of Harries and Schauwecker[7]) on the other, have resulted in the acceptance of two different chemical formulæ for natural citronellal, namely



Limonene form. Terpinolene form.

From the research of H. Rupe and A. Jäger[8]) which is referred to on p. 136 of the present *Report* it is also evident that citronellal constitutes a mixture of two chemically different bodies of the chemical structure set forth above. On the other hand, chemists are still greatly at variance on the question whether, as held by Tiemann and Schmidt[9]) and by Schimmel & Co.[10]). *l*-citronellol of geranium oil and rose oil and ordinary *d*-citronellol (from citronellal) represent merely two optically different modifications of one and the same alcohol, or whether Barbier and Bouveault[11]), Bouveault and Gourmand[12]), and Barbier and Léser[13]) are correct in assuming the two bodies to be alcohols of different constitution, namely rhodinol and citronellol. In continuation of previous investigations, P. Barbier and R. Locquin[14]) in a recent publication attempt to bring further proof to show that rhodinol and citronellol are alcohols of different constitution.

In this publication the authors mention a number of experiments in which citronellol has been converted into rhodinol. Taking as their starting point the acetic ester of ordinary *d*-citronellol and *l*-citronellol (rhodinol from oil of geranium or rose), the authors attach hydrogen chloride or hydrobromic acid to the double bond, and, as is to be expected, they obtain the same additive product according to the following equation: —



Citronellol. Rhodinol.

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[1]) *Report* November **1908**, 139. — [2]) *Report* April **1904**, 51; October **1913**, 59. — [3]) *Berl. Berichte* **29** (1896), 903; *Report* October **1896**, 88; *Berl. Berichte* **30** (1897), 22; *Report* April **1897**, 58. — [4]) *Berl. Berichte* **26** (1893), 2257. — [5]) *Berl. Berichte* **41** (1908), 2187; *Report* November **1908**, 185. — [6]) *Berl. Berichte* **32** (1899), 3367. — [7]) *Berl. Berichte* **34** (1901), 1498, 2981; *Report* October **1901**, 70; April **1902**, 90. — [8]) *Liebigs Annalen* **402** (1914), 149. — [9]) *loc. cit.* — [10]) *Report* October **1904**, 119. — [11]) *Compt. rend.* **122** (1896), 737, 793; *Bull. Soc. chim.* III. **23** (1900), 458; *Report* October **1900**, 76. — [12]) *Compt. rend.* **138** (1904), 1699; *Report* October **1904**, 118. — [13]) *Compt. rend.* **124** (1897), 1308; *Report* October **1897**, 66. — [14]) *Compt. rend.* **157** (1913), 1114.

This body, when treated with sodium acetate in glacial acetic acid solution and subsequent saponification, affords, according to the original material, either *d*- or *l*-rhodinol. In addition to this, the reaction results in 3,7-dimethyl-octanediol, the citronellol-hydrate or -glycol of Tiemann and Schmidt[1]). When citronellol is taken as the starting-point, it is possible to arrive at rhodinol by converting citronellal oxime into citronellic acid from primarily-produced citronellic acid nitrile, and converting the citronellic acid into the chloride of hydrochloride of rhodinic acid by means of thionyl chloride in benzene solution at water-bath temperature. By boiling the ester of this acid (b. p. 137 to 140°, 15 mm.) with sodium acetate, as described above, rhodinic ester is obtained. This body is reduced to the corresponding alcohol, rhodinol, with sodium and absolute alcohol, according to the method of Bouveault and Blanc. The easiest way of converting citronellol into rhodinol is by means of the glycol already referred to. This glycol also results from the reduction of hydroxycitronellic ester, a liquid which boils between 139 and 142° (13 mm.), and which is formed in fairly considerable quantities as a by-product in the esterification of citronellic acid with absolute alcohol and concentrated sulphuric acid. Less simple is the preparation of the glycol by prolonged shaking of citronellol with 30 p.c. sulphuric acid. When boiled with 5 p.c. sulphuric acid the glycol again gives off water and is converted into rhodinol. According to the author the alcohol prepared in this manner has a much more rose-like odour than has the citronellol, which is so to speak almost odourless. As another proof of the difference between rhodinol and citronellol, it is stated that, when oxidised, the first-named affords an aldehyde, rhodinal, of which the oxime differs from citronellal oxime in not yielding citronellic acid nitrile when treated with acetic anhydride, and subsequently citronellic acid when treated with alcoholic potash, but, in concordance with Bouveault's earlier experience, acetylmenthone oxime. It was found impossible to accomplish the converse reaction, that is to say, the conversion of rhodinol into citronellol.

We intend later on to deal in detail with this matter on the basis of results obtained by us from experiments on the same subject.

Linalool. E. Ferrario and M^lle^ Xiesopolska[2]) stated at the meeting of the Sociétés de chimie de Genève et de Lausanne, held on July 9, 1913 that they have succeeded in preparing linalool synthetically by reacting with vinylmagnesium bromide upon natural methylheptenone. Up to the present no further particulars of this synthesis appear to have been published.

Menthol. By heating dimethylcinnamic acid in the liquid form with twice the theoretical quantity of menthol, hydrogen chloride, being occasionally passed through, H. Rupe, H. Steiger and F. Fiedler[3]) obtained the methylester of this acid in the form of a colourless, viscous oil, boiling at 198° (14 mm.). The body thus obtained was not wholly pure; it still gave a faint chlorine-reaction.

p-Menthonol. A. Kötz[4]) reports a synthesis of methyl-1-*iso*propyl-4-*cyclo*hexanone-3-ol-2 (*p*-menthonol). He started from methyl-1-*iso*propyl-4-*cyclo*hexanone-3-carboxylate-4, which he converted into methyl-1-*iso*propyl-4-chloro-2-*cyclo*hexanone-3-carboxylate-4. By boiling with a hot saturated potash solution the chlorine of this

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[1]) *Berl. Berichte* **29** (1896), 907. — [2]) *Chem. Ztg.* **37** (1913), 1122. — [3]) *Berl. Berichte* **47** (1914), 71. — [4]) *Liebigs Annalen* **400** (1913), 55.

body was exchanged for hydroxyl, while at the same time the ester was saponified, with evolution of carbonic acid gas. The *p*-menthanone-3-ol-2 generated during this manipulation had b. p. 139° (17 mm.).

Borneol. For the purpose of differentiating between borneol and *iso*borneol, G. G. Henderson and I. M. Heilbron[1]), recommend the preparation of the *p*-nitrobenzoates of these alcohols. With this object in view they diluted the alcohol, after dissolving it in from 10 to 15 times its weight of pyridine, with the calculated quantity of *p*-nitrobenzoylchloride and heated the solution for some time on the water bath. The pyridine is removed by careful manipulation with sulphuric acid (under ice-cooling). The *p*-nitrobenzoate is washed with dilute sulphuric acid and, when dried, is recrystallised from alcohol. Bornyl *p*-nitrobenzoate melts at 137°, *iso*-bornyl *p*-nitrobenzoate at 129°. The borneol which is recovered from the ester melts at 208°, the *iso*borneol at 217°.

Aldehydes.

Citronellal. With the object of studying the influence of certain groups upon the rotation of optically active bodies from the simplest possible example, by employing a body with only one asymmetric carbon atom, H. Rupe[2]) has introduced aliphatic and aromatic residues into citronellal, by means of Grignard's reaction. This method affords in the first place secondary alcohols, from which unsaturated hydrocarbons can be obtained by the elimination of one molecule of water. It is to be taken into account that citronellal occurs in two different modifications, a limonene- and a terpinolene-form. An examination of the citronellal derivatives afforded proof of the simultaneous presence of both forms, inasmuch as the oxidations of ozone yielded in one case acetone peroxide and *β*-methyladipic acid, and in the other also ketonic acids, which latter must be derived from the limonene-form.

It would lead us too far to discuss the optical behaviour of the numerous citronellal derivatives and of their decomposition-products, and we will therefore limit ourselves to a tabulation of the properties of the alcohols and hydrocarbons described by the author: —

Citronellal and	afford	B. p.	Corresponding hydrocarbon	B. p.
Magnesium methyl bromide	2,6-Dimethylnonene-[3]) 2-ol-8	103 to 104° (9 mm.)	2,6-Dimethyl-2,7-nonadiene	61 to 62° (9 mm.)
Magnesium ethyl bromide	2,6-Dimethyldecane-2-ol-8[4])	114 to 115° (10 mm.)	2,6-Dimethyl-2,8-decadiene	81 to 82° (9 mm.)
Magnesium propyl bromide	2,6-Dimethylundecene-2-ol-8	124° (9 mm.)	2,6-Dimethylundecadiene-2,8	90 to 91° (8 mm.)
Magnesium allyl bromide	2,6-Dimethylundecadiene-2,10-ol-8	123 to 124° (10 mm.)	2,6-Dimethylundecatriene-2,8,10	94 to 95° (8 mm.)
Magnesium *cyclo*hexyl bromide	2,6-Dimethyloctene-2-ol-8-*cyclo*hexane-8	166 to 167° (10 mm.)	2,6-Dimethyloctadiene-2,8 (2,7)-*cyclo*hexane-8	142 to 143° (9 mm.)
Magnesium phenyl bromide	2,6-Dimethyloctene-2-ol-8-benzene-8	172° (9 mm.)	2,6-Dimethyloctadiene-2,7-benzene-8	131 to 132° (9 mm.)
Magnesium benzyl chloride	2,6-Dimethylnonene-2-ol-8-benzene-9	178 to 179° (9 mm.)	2,6-Dimethylnonadiene-2,8-benzene-9	159 to 160° (9 mm.)
Magnesium phenyl ethyl bromide	2,6-Dimethyldecene-2-ol-8-benzene-10	188 to 189° (9 mm.)	2,6-Dimethyldecadiene-2,8-benzene-10	163 to 164° (9 mm.)

[1]) *Proceed. chem. Soc.* **29** (1913), 381. — [2]) *Liebigs Annalen* **402** (1914), 149. — [3]) Comp. *Report* October **1907**, 156. — [4]) Comp. *Report* October **1910**, 156.

Aldehydes and hydroxyseleno-naphthene. R. Lesser and R. Weiss[1]), have obtained characteristic condensation-products by boiling the alcoholic or acetic solutions of certain aldehydes with hydroxyseleno-naphthene. With furfurol an orange-coloured mass with m. p. 145 to 147° was obtained, and with salicylic aldehyde small, brownish-yellow, lustrous rods, m. p. 206 to 207°. Œnanthol and citral yielded oily condensation-products, which were not investigated further.

Aldehydes and pyruvic acid. E. Lubrzynska and J. Smedley[2]) have condensed piperonal (heliotropin), anisic aldehyde, cinnamic aldehyde, and benzaldehyde in faintly alkaline solutions at ordinary temperature with pyruvic acid into β-unsaturated α-ketonic acids. Oxidation of these ketonic acids with the calculated quantity of hydrogen peroxide in a neutral solution afforded the corresponding β-unsaturated phenylolefinic carboxylic acids, carbonic acid being split off. When pyruvic acid and piperonal were left standing in an alkaline solution for 8 days at room-temperature, dihydroxymethylenebenzalpyruvic acid resulted; a body crystallising in yellow needles, m.p. 163°. By the same treatment, anisic aldehyde yielded methoxybenzalpyruvic acid, m.p. 130°, and cinnamic aldehyde, cinnamal pyruvic acid, in red crystals, m.p. 73°, which were slowly converted into a yellow modification with a m. p. of 103 to 104°.

Aldehydes, electrolytic reduction. About two years ago J. Tafel and W. Schepss[3]) described the electrolytic reduction of anisic aldehyde by means of cadmium cathodes. Schepss[4]) has now reduced certain other aldehydes by the same method. From œnanthol he obtained a liberal yield of *n*-heptane; benzaldehyde afforded toluene, protocatechuic aldehyde, homopyrocatechol; vanillin, creosol (homopyrocatechol-3-methylether; m. p. of the picrate 111 to 111,5°) and piperonal a previously unknown substance, homopyrocatechol methylenic ether, b. p. 197 to 198° (741,5 mm.).

Salicylic aldehyde. At the meeting of the American Chemical Society at Milwaukee on 24 to 28 March 1913, J. J. Skinner[5]) discussed the isolation and identification of salicylic aldehyde in the soil, and reported on experiments made with the object of determining the effect of this organic constituent of the soil upon the growth of vegetation. In cultivation experiments in nutritive solutions, salicylic aldehyde in a concentration of 1:100000 proved to be extremely detrimental to wheat, maize, cabbage and chick-peas; while in concentrations of 1:10000 to 1:20000 it was fatal to the plants. It was noxious in cultures containing phosphate, nitrate or potash, either by themselves or in combination. Its presence in the soil or in sand, even in small proportions, has a harmful effect. Skinner has tested 45 samples of non-productive and 30 of productive soils from various parts of the United States for the presence of salicylic aldehyde, and has found the substance to occur in 17 of the former and 3 of the latter.

Cinnamic aldehyde. N. Kishner[6]), in his work on the pyrazoline bases, refers to a conversion of cinnamic aldehyde into phenyl*cyclo*propane. Cinnamic aldehyde and hydrazine hydrate in absolute alcohol in the warm give rise to phenylpyrazoline (I),

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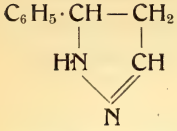
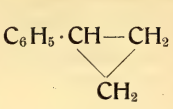
[1]) *Berl. Berichte* **46** (1913), 2640. — [2]) *Biochem. Journ.* **7** (1913), 375; *Chem. Zentralbl.* **1914**, I. 561. — [3]) *Berl. Berichte* **44** (1911), 2148. — [4]) *Ibidem* **46** (1913), 2564. — [5]) *Chem. Ztg.* **37** (1913), 1485. — [6]) *Journ. russ. phys. chem. Ges.* **45** (1913), 949, 957; *Chem. Zentralbl.* **1913**, II. 2129, 2130.

which, when heated with solid potassium hydroxide in the presence of platinised pieces of porous tile is converted into phenyl*cyclo*propane (II). The last-named body boils at 173,6°; $d_{0°}^{20°}$ 0,9401; $n_{D15°}$ 1,5342. When left standing with concentrated sulphuric acid it polymerises into a solid mass; if shaken for two days with dilute sulphuric acid it is converted into a dimeric phenyl*cyclo*propane, $C_{18}H_{20}$; b.p. 330 to 332°, $d_{0°}^{17°}$ 1,002.



(I) Phenylpyrazoline.



(II) Phenyl*cyclo*propane.

Ketones.

Methylheptenone. In continuation of their earlier investigations, G. Ciamician and P. Silber[1]) have studied the action of light upon methyl heptenone (I). The ketone was exposed to light from the end of May to the beginning of November in a capacious flask filled with oxygen. When the flask was opened a considerable vacuum was apparent, and instead of oxygen the vessel was found to contain carbon dioxide. A reaction-mass had been formed in the shape of a yellowish, strongly acid solution, from which acetone (bromophenyl hydrazone, m. p. 93 to 94°) was isolated. The solution was rendered alkaline with potash and extracted with ether, the result being a keto glycol (II) and possibly also a hydroxydiketone (III). For the purpose of identifying the latter it was converted into the diketone $(CH_3)_2CH\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$ by boiling with dilute sulphuric acid. The semicarbazone and the dioxime gave approximately the correct m. p. In the alkaline solution, when extracted with ether, and acidulated, formic acid, acetic acid, and lævulic acid were found.

(I) $(CH_3)_2C:CH\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$ Methylheptenone.

(II) $(CH_3)_2C(OH)\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$ Ketone glycol.

(III) $(CH_3)_2C(OH)\cdot CO\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3$ Hydroxydiketone.

Santenone. Some time ago we referred to a publication by Rimini[2]) on santenone, in which a new isomeride, *iso*santenone, was described. From its behaviour towards permanganate *iso*santenone would appear to be an unsaturated body, but in reality, as has now been established, it is saturated, as Rimini[3]) has discovered subsequently that the reaction of *iso*santenone with permanganate was caused by traces of impurities with powerful reducing-properties. For purposes of purification, the *iso*santenone was diluted with a 2 p. c. potassium permanganate solution under ice-cooling. The semicarbazone obtained from this product melts at 175° and, when decomposing, yields *iso*santenone, m. p. 185 to 186°. *Iso*santenone oxime constitutes a syrupy oil, b. p. 155 to 164° (28 mm.). Unlike santenone oxime, it readily reforms *iso*santenone when brought to boil with dilute sulphuric acid. Rimini also describes dibromo-*iso*santenone, as well as the oxidation of *iso*santenone. When treated with potassium permanganate in alkaline solution at ordinary temperature a syrupy compound $C_7H_{11}CO\cdot CO_2H$, is formed which, when heated with lead peroxide in glacial acetic acid solution, gives off carbon dioxide. The semicarbazone of the oxidation-product melts at 196°. Oxidation of *iso*santenone with potassium permanganate in alkaline solution in the warm,

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[1]) *Berl. Berichte* **46** (1913), 3077; comp. *Report* October **1911**, 122. — [2]) Comp. *Report* April **1912**, 185. — [3]) *Gazz. chim. ital.* **43**, II (1913), 522; *R. I. Lombardo di Scienze e Lettere* **46** (1913), 787 (courteously forwarded to us by the author); *Chem. Zentralbl.* **1913**, II. 1390.

or with sodium hypobromite, gives rise to a monobasic saturated acid $C_8H_{12}O_2$, m. p. 38 to 39°. The same acid is formed when dibromo-*iso*santenone is oxidised.

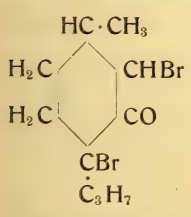
Menthone. On p. 142 of our last April *Report* we referred to methyl-3-menthanol-3, a body which has been prepared by J. Wanin. A. Arbusov[1]) now states this alcohol has already previously been decribed in detail by Zelinski and himself.

o-Menthone. A. Kötz[2]) describes an *o*-menthone-3 (methyl-1-*iso*propyl-2-*cyclo*hexanone-3). He reduced by Paal's method methyl-1-*iso*propyl-2-*cyclo*hexene-1-one-3, from which he obtained *o*-menthone-3, a liquid with a faint odour of peppermint; b. p. 204° (95 to 96° at 15 mm.). The semicarbazone melts at 204 to 205°; no oxime could be obtained[3]).

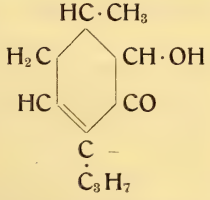
Dibromomenthanone. According to G. Cusmano[4]), the 1,9-dibromomenthanone-3 (dibromomenthone) described by Beckmann and Eickelberg is in reality a 2,4-dibromomenthanone-3 (I). That one bromine atom is in 4-position is evident from the fact that 2,4-dibromomenthanone-3 may also be obtained by brominating 4-monobromomenthone. On the other hand, the positton of the second bromine atom in 2 is proved by the conversion of dibromomenthone into buchu-camphor (diosphenol). When the dibromomenthone is shaken with 2,5 p.c. potash liquor until it is dissolved, and the liquid is then saturated with carbon dioxide, the result is buchu-camphor (m.p. 84°; semicarbazone, m.p. 219 to 220°). The only explanation of the reaction is that the bromine in 4-position is eliminated in the form of hydrobromic acid, whereas the bromine in 2-position is replaced by hydroxyl, giving rise to an unsaturated keto alcohol (II). This alcohol is then converted into a diketone (III) which, according to Semmler and Mac Kenzie, is readily converted into buchu camphor (IV). The action of bromine upon buchu camphor in chloroform solution gives rise to monobromo buchu camphor (m.p. 85°), which, when treated with a 2 p.c. aqueous potash liquor is converted into hydroxy thymoquinone.

When amines are allowed to react with dibromomenthone, one bromine atom is replaced by an imino-residue. Thus, with aniline the anilide, m.p. 195°, results. *β*-Hydroxyl amide melts between 158 and 160°.

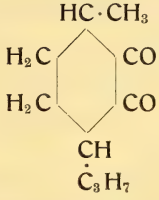
With nitrous acid dibromomenthone yields an *iso*nitramine $C_{10}H_{16}OBr \cdot N_2O_2H$, which is decomposed with great violence at 35° with evolution of red vapours.



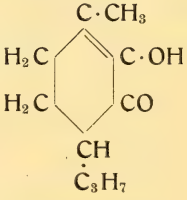
(I) 2,4-Dibromomenthanone-3.



(II) Unsaturated ketoalcohol.



(III) Diketone.



(IV) Buchucamphor.

Camphor. I. Bellucci and L. Grassi[5]) have closely investigated the camphor-sulphur dioxide system, with the object of determining the part which is played by

[1]) *Journ. russ. phys. chem. Ges.* **45** (1913), 700; *Chem. Zentralbl.* **1913**, II. 1482. — [2]) *Liebigs Annalen* **400** (1913), 85. — [3]) Comp. *Report* April **1911**, 182; April **1913**, 143. — [4]) *Atti R. Accad. dei Lincei* (5) **22**, II (1913), 569; *Chem. Zentralbl.* **1914**, I. 976. — [5]) *Atti R. Accad. dei Lincei* (5) **22**, II (1913), 676; *Chem. Zentralbl.* **1914**, I 978.

camphor in the preparation of sulphuryl chloride by Schulze's method (reaction of chlorine with sulphur dioxide in the presence of camphor). The authors have come to the conclusion that in this reaction camphor does not act as a catalyst, but that the compounds $2\,SO_2 \cdot C_{10}H_{16}O$, m.p. — 45° and $SO_2 \cdot C_{10}H_{16}O$, m.p. — 24° are formed as intermediary products, and that these on their part react with chlorine.

B. L. Vanzetti[1]) has ascertained that the absence of all thermic effect when the dilute solutions of the two active forms of the camphor oximes, which constitute a true racemate, are mixed together. He has thereby proved that in dilute solutions the racemate has become completely decomposed into the two optical antipodes.

Epicamphor. On p. 159 of our *Report* of October **1912** we referred to a paper on the preparation and properties of epicamphor, by J. Bredt and W. H. Perkin, published in the *Proceedings of the Chemical Society*. Since then the authors have published the experimental details of this investigation in other journals[2]), which fact enables us to complete our reference by the following particulars: —

The preparation of epicamphor may start with *d*-bornylene-3-carboxylic acid, which is converted from its primarily-produced chloride into the hydrazide and the azide. The last-named, when boiled with hydrochloric acid, affords *l*-epicamphor. A drawback of this method is the danger of explosion with which the preparation of the azide is attended. The preparation of epicamphor from *d*-bornylene-3-hydroxamic acid is therefore to be preferred. When heated above its melting-point the hydroxamic acid, with explosive rapidity, forms epicamphor, ammonia, water and a yellow-coloured resin. The mechanism of this reaction is probably as follows: bornylene-3-hydroxamic acid, when heated, loses water, and at the same time a molecular transposition takes place with formation of a resinous product consisting of bornylene-3-*iso*cyanate. The water which has been formed in the course of the reaction splits up part of the *iso*cyanate into ammonia and epicamphor. When the resin is treated with hydrochloric acid and distilled with steam, epicamphor is obtained by this method. The decomposition of acetyl- and benzoyl-*d*-bornylenehydroxamic acid is attended with less violence. When treated with toluene-*p*-sulphochloride these derivatives undergo transposition in the manner described under bornylenehydroxamic acid, giving rise to *l*-epicamphor. Unfortunately the preparation of *d*-bornylene-3-carboxylic acid takes a great deal of time and is very complicated, and epicamphor therefore remains a preparation which it is difficult to obtain. *l*-Epicamphor has the following characters: m. p. 182°, b. p. 213°, $[\alpha]_D$ — 58,21° (in benzene).

Singularly enough, the *l*-epiborneol which is formed in the process of reduction of *l*-epicamphor has no optical rotation. It is nevertheless no inactive substance, for it may be converted into *l*-bornylene (α_D — 18,45°) from the primarily-produced xanthogenate.

Epi*iso*borneol corresponding to *iso*borneol is as yet unknown.

Epicamphor is no more capable than common camphor of forming a cyanohydrin.

Epicamphocarboxylic acid is more readily reducible than is camphocarboxylic acid. Even when treated with sodium amalgam reduction takes place, although but slowly. By the electrolytic method[3]) reduction proceeds readily, with formation of four isomeric *l*-epiborneolcarboxylic acids, which differ from each other in their m. p. and their

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[1]) *Atti R. Accad. dei Lincei, Roma* V. **22** (1913), II. 379; *Chem. Zentralbl.* **1914** I. 145. — [2]) *Journ. chem. Soc.* **103** (1913), 2182. *Journ. f. prakt. Chem.* II. **89** (1914), 209. — [3]) Comp. *Report* April **1912**, 191.

optical rotation. When water is abstracted from a mixture of these acids by treatment with acetyl chloride, *l*-bornylene-2-carboxylic acid (m. p. 115°) is formed. This body is capable of being hydrogenated by means of hydrogen, in the presence of palladium and gum arabic, into *l*-camphane-2-carboxylic acid (m. p. 78 to 80°). Houben and Kesselkaul[1]) had already previously prepared epicamphane-2-carboxylic acid from pinene hydrochloride by converting the latter into the magnesium compound and treating with carbon dioxide. Houben called this acid hydropinenecarboxylic acid. Zelinsky[2]) also has already handled this acid, which he described as camphane carboxylic acid. *l*-Bornylene-2-methyl carboxylate reacts readily with hydroxylamine in the presence of sodium methylate, giving rise to *l*-bornylene-2-hydroxamic acid. The latter yields *d*-camphor when heated with hydrochloric acid and distilled by steam.

From the above it is clear that it is possible to convert *d*-camphor into *l*-epicamphor, and *vice-versâ*, according to the following arrangement: —

d-Camphor

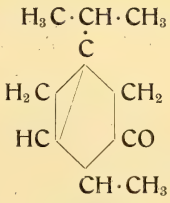
d-Camphocarboxylic acid — *l*-Bornylene-2-hydroxamic acid
d-Borneolcarboxylic acid — *l*-Bornylene-2-carboxylic acid
d-Bornylene-3-carboxylic acid — *l*-Epiborneolcarboxylic acid
d-Bornylene-3-hydroxamic acid — *l*-Epicamphocarboxylic acid

l-Epicamphor

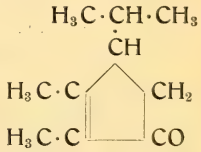
There remains to be mentioned the physiological action of epicamphor, which is decidedly weaker than that of its isomeride. About four times as much epicamphor as common camphor is required to produce an equal degree of acceleration of cardiac activity, while moreover the action of the epicamphor is much less sustained. In the same concentration which is required to produce a favourable effect with epicamphor, common camphor provokes toxic symptoms.

Fenchone. M. Saizeff[3]), when acting with zinc upon a mixture of fenchone and allyl iodide in the cold, obtained allyl fenchyl alcohol, a body which boils between 107 and 109° at diminished pressure. $d_{4°}^{20°}$ 0,9597; $[\alpha]_D + 12{,}44°$; n_D 1,40143. When hydrochloric acid was passed into it, the allyl fenchyl alcohol yielded a body $C_{13}H_{21}Cl$, b.p. 122 to 124.

Thujone. A few years ago we reported on a paper on alkylated thujones published by A. Haller[4]). Recently the same author has described new alkyl-derivatives of thujone and *iso*thujone[5]). He set out from the consideration that if the formulæ assigned to thujone (I) and *iso*thujone (II) are correct, thujone must be trebly and *iso*thujone doubly alkylatable, and he has in fact succeeded in preparing a triallylthujone and a dimethyl*iso*thujone. The *iso*thujone is much more difficult to alkylate than the thujone, and forms a considerable proportion of resin during the process.



(I) Thujone.



(II) *Iso*thujone.

[1]) *Berl. Berichte* **35** (1902), 3996; **38** (1905), 3796; *Report* April **1906**, 116. — [2]) *Berl. Berichte* **35** (1902), 4417. — *Journ. russ. phys. chem. Ges.* **34** (1902), 646. — [3]) *Journ. russ. phys. chem. Ges.* **45** (1913), 1578; *Chem. Zentralbl.* **1914**, I. 783. — [4]) *Compt. rend.* **140** (1905), 1626; *Report* October **1905**, 115. — [5]) *Compt. rend.* **157** (1913), 965.

In addition to the above alkyl-derivatives Haller has prepared a few others. We need say very little about the method of preparation. It is based upon the action of sodium amide upon the ethereal solution of the ketone and upon treatment of the product of reaction with alkyl halogenide, exactly as in the preparation of the alkyl menthones[1]).

Dimethylthujone . .	B.p. 92 to 94° (12 mm.);	$d_{4^\circ}^{15^\circ}$ 0,916;	$[\alpha]$ — 19° 45′	—
Diallylthujone . .	„ 147,5 „ 148,5° (18 mm.);	$d_{4^\circ}^{20^\circ}$ 0,9352;	—	n_{D20° 1,4850
Triallylthujone . .	„ 173 „ 175° (21 mm.);	$d_{4^\circ}^{20^\circ}$ 0,9467;	—	n_{D20° 1,5016
Dimethyl*iso*thujone .	„ 120 „ 122° (19 mm.)	—	—	—
Allyl*iso*thujone . .	„ 144 „ 146° (18 mm.);	$d_{4^\circ}^{20^\circ}$ 0,9280;	—	n_{D20° 1,4930.

Pulegone. M. Saizeff[2]) has prepared ethyl-3-pulegol from pulegone and ethylmagnesium bromide. The body boils between 112 and 115° (16 mm.); $d_{4^\circ}^{20^\circ}$ 0,9223; $[\alpha]_D$ + 43,22°. Oxidation with 1 p.c. potassium permanganate solution in the presence of magnesium sulphate in the cold, gave rise to formic acid, methyladipic acid (?), and possibly a body $C_{12}H_{24}O_3$.

Carvone and eucarvone. In his 116th monograph on terpenes and essential oils, O. Wallach[3]) describes the reduction of carvoxime and eucarvoxime with palladium hydrogen. When carvoxime is reduced with hydrogen in the presence of colloidal palladium and the supply of hydrogen is restricted to such an extent that only 1 molecule of hydrogen is supplied for every molecule of oxime, the result is not dihydrocarvoxime but a beautifully crystallising oxime, which, after repeated recrystallisation, melts between 66 and 67°, and when resolved with acids, affords carvotanacetone, which latter substance yields the normal carvotanacetoxime, m. p. 75°. At first the oxime with the low m. p. was regarded as a stereoisomeric modification of ordinary carvotanacetoxime. Closer investigation, however, showed that the oxime with m. p. 66 to 67° represented mixed crystals from active carvoxime (m. p. 72°) and active carvotanacetoxime (m. p. 75°), which are remarkably stable and do not even undergo a perceptible change in habit when repeatedly recrystallised. If, in the process of reducing carvoxime, the supply of hydrogen is not restricted, ammonia, carvacrylamine, and tetrahydrocarvone result, but no tetrahydrocarvoxime. This fact is worthy of note, because carvone is capable of being reduced to tetrahydrocarvone, and it follows therefore that the ethylene linkage does not readily dissolve when it occupies a position adjacent to an oxime-group. On the other hand, the vicinal position of the ethylene linkage appears to facilitate the attack upon the oxime-group of palladium hydrogen, and this is especially evident when carvoxime and carvotanacetoxime are severally treated with palladium hydrogen under precisely similar conditions. It would appear that the double-linking which exists in carvone conjugated with carbonyl is less easily reduced than the double-linking in the extra-cyclical position which is present at the same time, whereas the reverse is the case when the linkages in question are present in an isolated position, as in carvotanacetone and in dihydrocarvone. Thus, according to Vavon[4]), free carvone, when reduced with platinum black and hydrogen, yields first of all carvotanacetone, and only yields tetrahydrocarvone when the reduction has progressed further. Our present formulæ of molecular structure afford no explanation of these phenomena.

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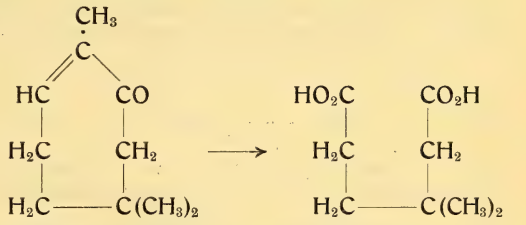
[1]) *Compt. rend.* **156** (1913), 1199; *Report* October **1913**, 146. — [2]) *Journ. russ. phys. chem. Ges.* **45** (1913), 1571; *Chem. Zentralbl.* **1914**, I. 783. — [3]) *Liebigs Annalen* **403** (1914), 73. — [4]) *Compt. rend.* **153** (1911), 68; *Report* October **1911**, 150.

In the reduction of eucarvoxime, as in that of carvoxime, the ultimate products which are obtained depend upon the experimental conditions. As a general rule, reduction proceeds more rapidly and is more thorough when concentrated methylalcoholic solutions are used, than with dilute solutions. Thus, for instance, the principal reduction-product of 5 grams eucarvoxime in 50 to 60 cc. methylalcohol in the presence of 0,05 to 0,1 grams colloidal palladium and 10 cc. water, is a previously unknown crystalline modification of tetrahydroeucarvoxime melting between 56 and 57°. The tetrahydroeucarvone regenerated from the oxime has normal properties[1]). So far it has not been possible to reconstitute the new oxime when the regenerated tetrahydroeucarvone is oximated. In contradistinction to the experience of von Baeyer, it was found that tetrahydroeucarvone affords without difficulty a readily-crystallising nitroso-compound, m. p. 104 to 105°. Tetrahydroeucarveol is obtained both by reducing tetrahydroeucarvone with sodium in alcoholic solution, and by reducing dihydroeucarveol with palladium and hydrogen. This tetrahydroeucarveol yields a phenylurethane with m. p. 74 to 75°. With the object of achieving partial reduction only, 15 grams of eucarvoxime were shaken in a hydrogen-atmosphere with 0,02 grams of colloidal palladium and 210 cc. of methylalcohol. The result was a new dihydroeucarvoxime, m. p. 122 to 123°, to which Wallach has given the name of β-dihydroeucarvoxime, to distinguish it from the previously-known dihydroeucarvoxime. β-Dihydroeucarvone boils between 213 and 214°, α-dihydroeucarvone at 205°. These two bodies differ also in their density, refraction, and the m. p. of their semicarbazones. Oxidation of β-dihydroeucarvone (I) with chromic acid leads to β,β-dimethyladipic acid (II). Distillation of the calcium-salt of this acid with soda lime in a hydrogen current afforded β,β-dimethyl *cyclo*pentanone (m. p. of the dibenzylidene compound 139°). From the above it follows that the structure of β-dihydroeucarvone is as shown in (I).



(I) β-Dihydroeucarvone. (II) β,β-Dimethyladipic acid.

In conclusion, Wallach communicates certain observations made by him on the dicarvelones and dieucarvelones, bodies which are formed when carvone or eucarvone is reduced with zinc and soda liquor. These bodies are diketones, and occur in several isomeric modifications. Wallach has now succeeded in clearing up, at any rate in certain directions, the uncertainties which have hitherto prevailed concerning the constitution and the mutual relationships of these compounds.

On the action of heat upon ketoximes, see p. 148.

Phenols and Phenol-ethers.

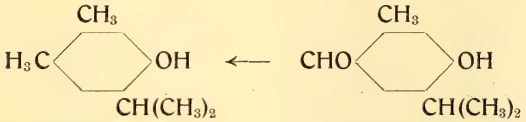
Phenol-ether, Reduction. In our last April *Report* (p. 133) we referred to the experiments in reduction under high pressure and in the presence of a catalyser carried on by W. Ipatieff. In his most recent publication, this investigator[2]) describes the reduction of the phenols with an unsaturated side-chain. By using reduced nickel as a catalyst under high pressure, saturation of the double bond takes place first, and only after this has been accomplished is the aromatic nucleus reduced.

[1]) Comp. *Report* April **1911**, 165. — [2]) *Berl. Berichte* **46** (1913), 3589.

Anethol, when reduced with hydrogen under a pressure of 50 atm. in the presence of reduced nickel, afforded at 95° dihydroanethol (b. p. 212 to 214°; $d_{20°}$ 0,9462). Hydrogenation of the dihydroanethol at 200° led to hexahydropropylbenzene (b. p. 160°). Hence the methoxyl-group was split off. Treated similarly, eugenol and *iso*eugenol afforded dihydroeugenol (b. p. 246°). When the reduction-process was continued a mixture of hexahydroanethol and octohydroeugenol resulted. Eugenolmethylether affords the dihydromethylether which, when further reduced, yields octohydroanethol, a methoxyl group being split off. Safrol and *iso*safrol yield dihydrosafrol (b. p. 228 to 230°) and, upon further reduction, in all probability an isomeric hexahydroanethol.

Thymol. K. Fries, W. Gross-Selbeck and O. Wicke[1]), in a voluminous paper, communicate the results of their researches into the *o*-pseudobromides of thymol and *o-iso*propylphenol, and their conversion into cumarane derivatives. The manner in which the numerous preparations were obtained, and the preparation of characteristic derivatives are accurately described.

Methylthymol. In a communication by E. Clemmensen[2]) on a general method of reduction of the carbonyl group of aldehydes and ketones into the methylene group, we find a description of the preparation of *p*-methylthymol from *p*-thymotine aldehyde.



p-Methylthymol. *p*-Thymotine aldehyde.

25 grams of the aldehyde, 150 grams of amalgamated zinc and 400 cc. of dilute hydrochloric acid (1 : 1) were heated for 3 hours with frequent addition of further quantities of acid of the same strength. The reaction product, when driven over by steam, solidified into a white, crystalline mass, which was purified by distillation (b. p. 250 to 250,5° at 745 mm.) and recrystallisation from light petroleum. Pure *p*-methylthymol melts at 70°. It has a pleasant odour, which differs altogether from that of thymol.

Phenol allylethers. In our last April *Report* (p. 144), we mentioned a paper by L. Claisen on the conversion of phenol allylethers into *C*-allylphenols. Claisen and O. Eisleb[3]) have recently published a very detailed treatise on the same subject, from which we make the following excerpts which specially concern our particular sphere of interests. Conversion takes place as soon as the allylether is heated; as a rule a temperature below b. p. suffices to bring it about; only occasionally is it necessary to heat to b. p. A temperature of between 230 and 250° may be taken as the most favourable average for the conversion. The allylether of ordinary eugenol (b. p. 140° at 9 mm.; $d_{15°}$ 1,024) affords at b. p. immediately and at 200° within about half an hour, about 70 p. c. *o*-allyleugenol (*o,p*-diallylguajacol), a water-white oil with an odour resembling that of eugenol, but much fainter than the latter: b. p. 149° (10 mm.), $d_{15°}$ 1,036. In the process of conversion of guajacol allylether *o*-eugenol (*o*-allylguajacol) is, in fact, formed. *o*-Eugenol allylether boils at 128° (10 mm.). When *o*-eugenol is treated with potash in the warm the solid propenyl derivative, *o-iso*eugenol (*o*-propenyl guajacol) is formed: m. p. 78°. This body is identical with that obtained from *o*-vanillin and ethyl iodide by Pauly and von Buttlar[4]). It is possible greatly to

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[1]) *Liebigs Annalen* **402** (1914), 261. — [2]) *Berl. Berichte* **47** (1914), 62. — [3]) *Liebigs Annalen* **401** (1913), 21. — [4]) *Ibidem* **383** (1911), 282.

simplify the method of preparing *o*-eugenol by omitting the preliminary distillation of the guajacol allylether. Conversion of *o*-eugenol allylether results in the same *o,p*-diallylguajacol, which is obtained in the form of a conversion-product of the allylether of common eugenol. The allylether of salicylic aldehyde, when boiled, affords readily and exclusively 3-allyl salicylic aldehyde. From the technical product, this salicylic aldehyde can easily be prepared in the pure state by means of the primarily-produced copper-salt. Heating the *o*-vanillin allylether gives rise to a mixture of *o*-eugenol, allyl-*o*-vanillin, and allyl-*p*-vanillin. The allylether of common *p*-vanillin, when heated, yields 5-allylvanillin, m. p. 85 to 86°.

Acids.

Dihydrocamphoceenic acid. S. V. Hintikka[1]) has resolved dihydrocamphoceenic acid by a simple method into *iso*propyl*cyclo*pentanone. He treated the acid with phosphorus pentachloride and, when the reaction was completed, added the calculated quantity of bromine. The brominated acid was converted into hydroxydihydrocamphoceenic acid, which, when oxidised with peroxide of lead in acetic solution, afforded *iso*propyl*cyclo*pentanone (apocamphenilone), b. p. 78 to 79° (11 mm.). The semicarbazone had m. p. 198°.

The conversion of dihydrocamphoceenic acid amide into *β-iso*propyl*cyclo*pentanone had already been carried out previously by L. Bouveault and G. Blanc[2]), albeit by a more complicated method.

Camphane carboxylic acid. P. Barbier and V. Grignard[3]) have discovered interesting conditions of isomerism in camphane carboxylic acid (hydropinene carboxylic acid)[4]). This acid was prepared from pinene hydrochloride by the aid of Grignard's reaction. It now appears that pinene hydrochloride apparently exists in two modifications. The B-modification is formed when an alcoholic pinene solution, warmed to 75 to 80°, is saturated with dry hydrogen chloride. A liquid substance is then formed from which a solid hydrochloride can be obtained by fractional distillation *in vacuo*. The A-modification of pinene hydrochloride is obtainable by passing hydrochloric acid through pinene in the cold. By this method pinene from French turpentine oil ($[\alpha]_D$ — 35,17°) afforded a B-hydrochloride, with m.p. 126° ($[\alpha]_D$ — 21,66°) and an A-hydrochloride with m.p. 127° ($[\alpha]_D$ — 25,20°). The ethyl-magnesium compound of the B-hydrochloride yielded a labile dextrorotatory acid with m.p. 76 to 78°, b.p. 157 to 158° (16 mm.), which was converted into stable lævorotatory *α*-camphane carboxylic acid (*l*-bornyl carboxylic acid), m.p. 88 to 89° by heating it with or without the addition of alcoholic potash liquor, aromatic amines or strong acids. From the A-hydrochloride the authors obtained a labile lævorotatory acid (m.p. 73 to 74°) which was convertible into a lævorotatory stable acid, m.p. 86 to 87° and which is most probably identical with the *α*-camphane carboxylic acid, m.p. 88 to 89°, referred to above. From inactive B-pinene hydrochloride the authors obtained a labile racemic acid (Houben's hydropinene carboxylic acid), m. p. 78 to 80°, which was converted into the stable r-camphane carboxylic acid, m.p. 93 to 94°.

Of all the acids only the stable ones, formed by the isomerisation of the labile acids, were fairly pure, all the labile acids were presumably mixtures.

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[1]) *Ann. Acad. Scient. Fennicæ.* A. V. No. 2 (1914), p. 3. From a reprint kindly sent to us. — [2]) *Compt. rend.* **146** (1908), 233; *Report* April **1908**, 191. — [3]) *Bull. Soc. chim.* IV. **15** (1914), 26. — [4]) Comp. *Report* October **1913**, 150.

Without entering into experimental details, we may here refer to a paper by J. Houben and E. Willfroth[1]) on camphene carboxylic amides and hydrocamphene carboxylic amide[2]). Chloro-*allo*-camphane carboxylic amide, when simply boiled with water, loses all its chlorine in the form of hydrogen chloride and is converted into an unsaturated amide: camphene carboxylic amide. Fuming hydrochloric acid re-converts the amide into the original substance. Reduction by means of platinum and hydrogen by Fokin-Willstätter's method causes the camphene carboxylic amide to become hydrogenated into a saturated compound which differs altogether from *allo*-camphane carboxylic amide and may possibly be identical with hydrocamphene carboxylic amide. Houben and Willfroth converted the acid mixture which had been obtained from chloro-*allo*-camphane carboxylic ester by treatment with methylalcoholic potash into the acid chlorides (using thionyl chloride) and treated these acid chlorides with ammonia. By this method they obtained various amides, including two isomeric unsaturated amides, of which one (m. p. 209°) proved to be identical with camphene carboxylic amide. In conclusion the authors attempted to saponify the amide which they had obtained by the hydrogenation of camphene carboxylic amide into hydrocamphene carboxylic acid, but this experiment resulted in an acid, m. p. 126°, which differed from *allo*camphane carboxylic acid: possibly a hydrocamphene carboxylic acid or *iso*camphane carboxylic acid.

Hydroxycamphenilanic acid. The lead salt of hydroxycamphenilanic acid (camphenylic acid), when subjected to dry distillation, gives rise to a yellow diketone $C_{10}H_{14}O_2$, to which S. V. Hintikka[3]) gives the name carbocamphenilone. This body occurs in lemon-yellow prisms, m.p. 58 to 59°. When oxidised with hydrogen peroxide it is converted into an acid, m.p. 136°; which is most probably identical with camphene camphoric acid.

Cinnamic acid. H. Stobbe and C. Schönburg[4]) believe that, as the result of a thorough investigation into the subject, they have solved the problem of the chemical difference[5]) between allocinnamic acid with m. p. 67° and the two *iso*cinnamic acids melting respectively at 58 and 42°. The solutions of the three acids differ, because under stated conditions they are capable of being recrystallised without undergoing change, and because it is possible to prepare unequal solution-mixtures of any two of the acids. The 68°- and the 58°-acids undergo chemical changes during melting. The constitution of the mixtures is regularly dependent (apart from the nature of the melted acid), upon the period and the temperature of the heating of the fluxes. The preparations which result when the solution mixtures are evaporated and when the fluxes solidify, melt respectively at 68°, 58° or 42°. The 68°-preparations constitute practically pure *allo*cinnamic acid. The 58°- and the 42°-acid preparations do not constistitute uniform *iso*cinnamic acids, but crystal-mixtures (solid solutions) of two or three acids, in which the acid with the lowest b. p. which is present in excess, always acts as the solvent.

The miscibility (*i. e.* the solubility) of the solid acids with higher m. p. is restricted. It follows therefore that saturated, unsaturated and super-saturated solid solutions must exist, and hence that the 58°- and the 42°-acid preparations may also differ quantitatively. The 58°- and the 42°-crystal mixtures are capable of being segregated, the

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[1]) *Berl. Berichte* **46** (1913), 2530. — [2]) Comp. *Report* October **1913**, 150. — [3]) *Berl. Berichte* **47** (1914), 512. — [4]) *Liebigs Annalen* **402** (1914), 187. — [5]) Comp. *Report* October **1906**, 150; April **1907**, 155; April **1909**, 138; October **1909**, 210; April **1910**, 188; October **1910**, 203; April **1912**, 192.

acids with higher m. p. being separated out. Such a result may be caused merely by a lowering of the temperature, or by the spontaneous conversions.

From the dissimilarity of the solutions and fluxes, the existence of dissimilar solution- and flux-mixtures, and from the laws which govern the conversion of the systems from solid $\longrightarrow$ liquid, and from solid $\dashrightarrow$ solid, it follows unequivocally that the *allo-* and the *iso*cinnamic acids are three bodies of chemically different character. The *allo-* and *iso*cinnamic acids do not constitute three genera of a trimorphous *cis*-cinnamic acid; on the contrary, each of the three is in itself isomeric with ordinary cinnamic acid of m. p. 133°.

It remains to be considered that the chemical difference of these four isomerides cannot be made clear by the usual stereo-chemical formulæ, seeing that, up to the present, only two symbols are available, namely:

$$\begin{matrix} C_6H_5\cdot\dot{C}\cdot H \\ HO_2C\cdot\ddot{C}\cdot H \end{matrix} \quad \text{and} \quad \begin{matrix} C_6H_5\cdot\dot{C}\cdot H \\ H\cdot\ddot{C}\cdot CO_2H. \end{matrix}$$

Oxides.

Cineol. I. Bellucci and L. Grassi[1]) believe that in the present state of our knowledge of the oxonium salts it is advisable to regard these substances as simple molecular additive compounds. The authors have investigated the power of combination of a series of organic compounds with one single substance, paying special attention to the influence of position isomerism upon this property of combination. They selected cineol as an oxygenated compound because it exhibits a marked tendency to form additive compounds, because it is a good solvent for many bodies, and, finally, because its solidifying point (+ 1°) is specially suitable for thermic analyses.

They were unable to examine the cineol-carvacrol system because the mixture refused to crystallise at a low temperature. They were unable to confirm by thermic analysis the existence of a combination of cineol and resorcinol, but thy were able to prove the existence of an additive compound with α- and β-naphthol. The compound with α-naphthol melts between 73 and 75°, that with β-naphthol between 48 and 50°. Additive compounds were also obtained from one molecule of cineol with one molecule each of phenol (m.p. + 8°), *o*-cresol (m.p. 50°), *m*-cresol (m. p. — 5°), *p*-cresol (m. p. 1,5°), pyrocatechol (m. p. 39°), resorcinol (m. p. — 15°), thymol (m. p. + 4,5°), and from two molecules of cineol with one molecule of hydroquinone (m.p. 106,5°). A compound with *p*-hydroxybenzoic acid appears to exist, but it is decomposed before melting. Cineol does not combine with *o*-, *m*- and *p*-nitrophenol; *o*- and *m*-amidophenol, *o*- and *m*-hydroxybenzoic acid and with phenyl- and naphthyl-salicylate. The results obtained appear to afford evidence against the theory of the oxonium salts and the basic character of the oxygen, because, although phenol is absorbed, the more strongly acid nitrophenols are not.

Nitrogenous bodies.

Alkylidene hydrazines. In continuation of his earlier investigations[2]), N. Kishner[3]), has described the conversion of the hydrazine compound of methylheptenone into 1,1-dimethylhexene-1 when heated with potassium hydroxide. The hydrocarbon boils at 122,4°: $d_{0^\circ}^{20^\circ}$ 0,7254. The nitrosochloride melts between 48 and 51°.

[1]) *Gazz. chim. ital.* **43** (1913), II. 712; *Chem. Zentralbl.* **1914**, I. 884. — [2]) Comp. *Report* April **1193**, 152. — [3]) *Journ. russ. phys. chem. Ges.* **45** (1913), 973; *Chem. Zentralbl.* **1913**, II. 2132.

Ketoximes. A. Kötz and O. Wunstorff[1]) have investigated the action of heat upon ketoximes with the following oximes: acetoxime, benzophenone oxime, acetophenone oxime, desoxybenzoine oxime, *cyclo*hexanone oxime, benzoin oxime, methyl-1-*iso*nitroso-4-*cyclo*hexanone-3 and *iso*nitroso camphor. The action of heat in a dry current of carbon dioxide has the following effects: 1. distillation or sublimation of the oximes without decomposition; 2. decomposition into ketone, nitrogen and ammonia (ketone-decomposition); 3. decomposition into nitriles and alcohols (nitrile-decomposition). At 240° *iso*nitrosocamphor showed nitrile-decomposition as well as ketone-decomposition, the following decomposition-products being obtained: dimethyl-heptylenic acid nitrile, camphoric acid anhydride, and ammonia.

Benzyl*iso*sulphocyanide. In a lecture delivered before the 85th Congress of German Naturalists and Physicians held at Vienna, Schneider[2]) also stated that he had made attempts to isolate the glucoside of benzyl*iso*sulphocyanide which occurs in common garden cress. Although he had not yet completed his experiments, he had already ascertained that the sugar-constituent of the glucoside of garden cress (*Lepidium sativum*, L.) represents grape-sugar. The glucoside of Indian cress, however, does not contain grape-sugar but a polysaccharide which is incapable of being reduced and which has not yet been closely identified.

[1]) *Journ. f. prakt. Chem.* II. 88 (1913), 519. — [2]) *Chem. Ztg.* 37 (1913), 1169.

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on

Essential Oils,

Synthetic Perfumes, &c.

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Contents.

	Page
Introduction	5
Scientific notes on essential oils	6
Novelties	51
Chemical preparations and drugs	55
Notes on scientific research in the domain of the terpenes and essential oils.	
General	63
Bibliography	67
Analytical	68
Physical	72
Pharmaco-physiological	74
Phyto-physiological	78
Chemical	80
Hydrocarbons	82
Alcohols	89
Aldehydes	91
Ketones	95
Phenols and Phenol-ethers	101
Acids	105
Oxides	108
Nitrogenous bodies	108

List of abbreviations.

d = specific gravity.
$d_{20°}$ = specific gravity at 20° (in references from our laboratories uniformly compared with water at 15°).
$d^{20°}_{4°}$ = specific gravity at 20°, compared with water at 4°.
$\alpha_{D20°}$ = optical rotation at 20°, in a 100 mm. tube.
$[\alpha]_D$ = specific rotation.
$n_{D20°}$ = refractory index at 20°.
sol. p. = solidifying point.
m. p. = melting point.
b. p. = boiling point.
n = normal.
acet. = acetylation.
acid v. = acid value; ester v. = ester value; sap. v. = saponification value.
g. = gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent by volume.

Miltitz near Leipzig, April 1915.

If, for the first time since its inception, we refrained from publishing our *Report* in the usual way last October, there were several reasons for our action. Apart from the fact that the major part of our German readers were probably at the front and that those left behind to fight the economic battle of the nation had little leisure for reading, we were unable since the beginning of the war to collect the necessary statistical material from abroad about the various oils and raw materials, which originate mostly from foreign countries. Our silence was due in no small degree to the fact that even the most trivial publication of ours finds its way into the alien enemy's technical press. We consider that we should render a bad service to our trade, were we to furnish our enemies with any indications as to the influence of the war on our commerce and industry, on the reaction on our production, on stocks and supplies of raw material and finished articles and the possibility, or otherwise, of replenishing the former in view of the blockade from every side, or of turning over the latter. All informations on these important questions would no doubt be highly welcomed by our enemies, as they would enable them to arrange their tactics accordingly in the economic part of the war, the more so as even our enemies had to recognize for decades the reliable tenor of our publications. We are firmly convinced, an opinion which does not unfortunately appear to be appreciated in certain quarters in our own country, that the greatest possible reticence is required in compiling commercial reports during the present war, so that our opponents, who procure such reports with comprehensible eagerness, should be left entirely in the dark about all the events and incidents within the scope of German commerce and industry, whether they be favourable to us or otherwise. We go so far as to maintain that even after the re-establishment of peace, an event which we trust is not too far off, all and every statement as to influence and effect of the war on Germany's commerce and industry should be avoided which might enable our antagonists and revilers to draw conclusions about the weal and woe of our trade during the war.

As our hope for peace did not materialize so far, we decided, in order to obviate too great an accumulation of matter, to allow the scientific part of our *Report* to make its appearance without any further delay, but we refrain, for the reasons stated above, from enlarging upon matters commercial and economic, or on market conditions or any other incident in our department of German industry during war time.

May we be in a position to resume our *Reports* in the old manner before long!

SCHIMMEL & Co.

Scientific Notes on Essential Oils.

Ageratum Oil. Many years ago this oil had been distilled by van Romburgh[1]) from material collected in Buitenzorg. Roure-Bertrand Fils[2]) give the following properties for an Ageratum oil received by them from Annam: $d_{15°}$ 1,1090; α_D — 1° 20′; acid v. 0,9; ester v. 11,2; almost completely soluble in 5 volumes and more of 80 p.c. and in 0,5 vol. of 90 p.c. alcohol. The yield was 0,0054 p.c. According to Murat, *Ageratum conyzoides,* L. (N. O. *Compositae*) grows so freely as to constitute a pest for the planter in Annam. Distillation is started at the beginning of February or March.

Almond Oil, bitter. In an English contemporary[3]) the following method is recommended for the chlorine test in bitter almond oil. A piece of metallic sodium, about the size of a pea, is dropped into 1 cc. of bitter almond oil in a dry test tube, the whole being heated until all chemical action has ceased. The test tube and contents are immersed, whilst still hot, in a porcelain dish containing 10 cc. of distilled water. The solution is filtered, acidulated with nitric acid, and silver nitrate solution is added. Turbidity or opalescence indicates the presence of chlorine compounds; a blank test should be performed to ensure the absence of chlorine in the materials used.

This test is said to be even more sensitive than our combustion process. At all events its author claims that an artificial benzaldehyde, which had been found to be free from chlorine according to the latter method, showed a distinct chlorine reaction on being subjected to the first-named test.

On our making comparative tests we failed to make such observations, but we may say at once that this new test has the decided disadvantage of being more complicated than the combustion process. Moreover, with bitter almond oil containing prussic acid a strong precipitation of cyanide of silver takes place, which only disappears after prolonged heating of the mixture.

On the occurrence, in the Vegetable Kingdom, of glucosides hydrolysable with emulsin, see page 79.

On amygdalin contents of apricot kernels, see page 80.

Amber Oil. About the composition of amber oil, which — strictly speaking — does not belong to the group of essential oils at all, all that was known so far was that, besides a terpene mixture, it contained other hydroaromatic hydrocarbons, but no clear proof of the existence of these bodies had been adduced. Of late, however, more knowledge has been gained about the composition of the oil, A. Károly[4]) having examined a rectified oil of amber which contained about 5 to 8 p.c. of acids and esters, besides hydrocarbons. The acids consisted of higher fatty acids which were removed by shaking with dilute alkali. On being fractionated over sodium, under

[1]) *Report* April **1898**, 53. — [2]) *Berichte von Roure-Bertrand Fils* April **1914**, 8. — [3]) *Perfum. Record* **5** (1914), 264. — [4]) *Berl. Berichte* **47** (1914), 1016.

atmospheric pressure, the bulk of the oil boiled from 154 to 177°, and from 240 to 260°. The lower boiling portions yielded hydrogen haloid addition products which were not obtained in solid form. Under the influence of bromine vapours in the cold evolution of hydrogen bromide was observed. After the elimination of the oily parts a body of the formula $C_9H_9Br_3$ was obtained which, on recrystallization from ligroin, melted at 242°, being probably identical with tribromohemimellithene. Károly is of opinion that this latter body results from the bromination of a dihydrohemimellithol contained in the terpene fraction. Inasmuch as in the process of oxidation of the terpene fraction *i. a.* 1,3-dimethylterephthalic acid was obtained, it may be assumed that a dihydro-*iso*durene is probably present in amber oil. The same treatment applied to the sesquiterpene fraction produced a body of the melting point 254 to 256°. By hydration of the terpenes, after Bertram and Walbaum, Károly obtained an alcohol strongly resembling borneol but differing from it in the melting point of its hydrogen phthalate (118 to 119°). This body is probably identical with the one obtained by Berthelot and Buignet[1]) when distilling powdered amber with caustic potash and water. The hydrogen phthalate, prepared for comparison purposes from borneol of commerce, melted at 164 to 165°. The phenylurethane of the borneol-like alcohol obtained from the terpenes melted at 137 to 138°. On being oxidized with chromic acid the terpene alcohol yielded what was probably camphor (semicarbazone, m. p. 232°) which was converted into camphene by splitting off water. Amber oil, oxidized with a 1 p. c. solution of permanganate, yielded an acid which is probably identical with heptoic acid. Nitric acid reacts very slowly in the cold, but very energetically when heated, forming a mixture of two acids, one being terephthalic acid and the other a body most likely identical with 1,3-dimethylterephthalic acid. The formation of this acid points to the probable presence of a yet unknown 1,2,3,5-tetramethyldihydrobenzene (dihydro-*iso*durene). From the nitric acid mother liquor a further acid was obtained, which may possibly be identical with 2-nitro-p-toluic acid.

Ambrette (musk) seed Oil. Absolute proof that the solid fatty acid present in this oil was identical with palmitic acid[2]) had not been adduced so far. Recently we had an opportunity of establishing this proof. As raw material we used the crude acid which had been obtained as a by-product in the manufacture of liquid oil of ambrette seeds. As it appeared to be mixed with some other substance (fatty acid ester?) it was recrystallized several times from dilute alcohol. The glossy laminae melted at 61° and, when mixed with palmitic acid from coco-nut oil, showed no depression of the melting point. The silver salt of the acid yielded the following values upon incineration: —

0,3270 g. subst.: 0,0958 g. Ag.

found 29,30 p. c. calculated for $C_{16}H_{31}AgO_2$ 29,75 p. c.

Ammoniacum Oil. Little being known about Ammoniacum oil, we give the following figures of an oil obtained by ourselves (yield 0,19 p. c.): $d_{15°}$ 0,8875; $\alpha_D + 1° 37'$; $n_{D20°}$ 1,47250; acid v. 3,7; ester v. 40,5; ester v. after acetylation 106,4; soluble in 0,5 volume and more of 90 p. c. alcohol. The oil was of a dark yellow colour; it had a peculiar and rather unpleasant odour.

Angelica Oil. About cultivation experiments in Austria, see page 63.

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[1]) *Compt. rend.* 50 (1880), 606. — [2]) *Schimmel's Bericht* October 1887, 35.

Anise Oil, Russian. In our *Reports*[1]) we have repeatedly pointed out the advantages of Pharmacopoeias adopting, as far as possible, the active principles in place of the essential oils. In this respect we mentioned that anethol should take the place of Russian anise oil; the usefulness of the former is once again pointed out by O. Raubenheimer[2]). As we had done before, he states that one decided advantage of anethol is to be found in its being a uniform body of always uniform composition which can be examined for quality and purity far more closely than anise oil. Moreover, its taste is sweeter and its odour far more pleasant than the best anise oil, and from a therapeutical point of view it is more advantageous, as it constitutes the medicinally active part of anise oil. The price, too, is more in accordance with its strength than is the case with anise oil. As regards the proper use of anethol in the manufacture of *Liquor Ammonii anisatus,* Raubenheimer, in his experience extending over many years, always found it to yield a clear and colourless solution, whereas with anise oil yellow discoloration and turbidity often occur, the latter ending in precipitation. He also observed that many anise oils dissolved in 5 to 6 parts of 90 p.c. alcohol only, whereas 2 volumes sufficed for a solution of anethol. We might add, that so far we have never come across such badly soluble anise oils, and that in our opinion Raubenheimer must have had to deal with adulterated oils.

Oil of Artemisia arborescens. The oil distilled by us some years ago from dried herb of *Artemisia arborescens,* L. (N. O. *Compositae*)[3]) has now been examined more closely by T. Jona[4]). It contained 13,94 p.c. of alcohols $C_{10}H_{18}O$, free as well as in the form of esters, two of which were proved to be borneol (m. p. 203 to 205°; b. p. 212°) and thujyl alcohol (b. p. 211 to 212°; oxidation to thujone). The oil also contained 13 p.c. of β-thujone ($[\alpha]_{D210} + 76{,}02°$), which boiled from 200 to 202° and yielded a tribromide melting at 122°. In the saponification lyes a mixture of fatty acids was present, presumably formic, acetic, *iso*valeric, pelargonic, palmitic and stearic acids.

Oil of Buchu Leaves. The following table shows the exports of buchu leaves from South Africa during the years 1907 to 1912[5]):—

1907	291 334 lbs.,	value £	9 201	1910	273 325 lbs.,	value £	24 428
1908	243 472 „	„	„ 7 284	1911	212 082 „	„	„ 29 647
1909	260 126 „	„	„ 9 666	1912	223 021 „	„	„ 38 264

The highest price (6/6 lb.) was paid in London in 1912 for selected leaves of *Barosma betulina.*

The exports from the various ports were as follows in 1912:—

From Cape Town . . .	221 338 lbs.,	value £	38 166
„ Port Elizabeth . .	51 „	„	„ 2
„ Mossel Bay . . .	1 632 „	„	„ 96
	223 021 lbs.,	value £	38 264

Oil of *Barosma venusta.* This oil, the composition of which H. R. Jensen[6]) investigated some time ago, has been examined recently by E. Goulding and

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[1]) See *i.a. Report* April **1911**, 125, 127. — [2]) *Americ. Perfumer* **9** (1914), 22. — [3]) *Report* November **1908**, 136. — [4]) *Ann. Chimica appl.* **1** (1914), II. 631. — [5]) *Kew Bull.* **1914**, 194. — [6]) *Pharmaceutical Journ.* **90** (1913), 60; *Report* April **1913**, 34.

O. D. Roberts[1]). It had been obtained from the leaves to the extent of about 2 p.c. $d_{15°}$ 0,865; $\alpha_{D22°}$ +0° 47′; acid v. 5,6; ester v. 6,2; ester v. after acetylation 55. 43 p.c. of the oil consisted of myrcene. The other component parts were: about 0,5 p. c. of anisic aldehyde, about 10 p.c. of linalool, 21,4 p.c. of methylchavicol and 18,4 p.c. of sesquiterpenes and decomposition products. The abstract in question does not state in which manner the presence of these bodies was proved.

Cajuput Oil. For a cajuput oil distilled in Annam from the stalks and leaves of *Melaleuca Leucadendron* Roure-Bertrand Fils[2]) give the following values: $d_{15°}$ 0,9198; α_D −2° 36′; soluble in 1,8 volumes of 70 p. c. and in 0,5 volume and more of 80 p.c. alcohol. The oil contained 40,5 p. c. of cineol (resorcinol method).

Calamus Oil. Japanese calamus oil is closely related to the German distillate in its chemical constants and really differs from it only in its being specifically heavier. Within the last year, however, we repeatedly received samples of laevo-rotatory oils from Japan, whereas so far we had only observed dextro-rotation, same as in oils of German origin. In all other respects these Japanese oils showed quite normal constants, and possessed a good odour: $d_{15°}$ 0,9846 to 0,9863; α_D −5° 36′ to −11° 25′; $n_{D20°}$ 1,51655 (one single test); acid v. 0,9 to 1,1; ester v. 1,3 to 9,1; soluble in about 2 volumes of 80 p. c. and in 0,4 volume or even less of 90 p. c. alcohol.

It could not be established how this difference in the rotation was to be explained, at any rate no indication pointing to adulteration could be found. Most likely the oils in question were obtained from a different species of calamus. According to Holmes[3]), *Acorus spurius,* Schott is very prevalent in Japan, its rhizome being said to be hardly distinguishable from the true *Acorus Calamus,* L. In the *Index Kewensis,* however, both are spoken of as being identical.

Oil of Calycanthus floridus. *Calycanthus (Butneria) floridus,* L. (N.O. *Calycanthaceae*) is an aromatic, small-sized shrub indigenous to northern America, and as an ornamental plant it is also met with in Europe. From its dry twigs, which had already lost nearly all their leaves, E. R. Miller, G. W. Taylor and M. H. Eskew[4]) obtained from 0,25 to 0,53 p. c. of a light yellow essential oil with an odour resembling camphor. $d^{25°}_{25°}$ 0,9136 to 0,9209; α_D +2,84 to +6,6°; $n_{D26°}$ 1,4675 to 1,4753; sap. v. 12,5 to 16,6; sap. v. after acetylation 65,7 to 75,1; soluble in 16 to 25 volumes of 70 p. c. and in every volume of 90 p. c. alcohol. Aldehydes, ketones and phenol ethers were either not present at all, or in traces only, but the oil contained a fair amount of cineol (iodol compound, m. p. 111°), as well as salicylic acid (?) (colour reaction with ferric chloride) and α-pinene (nitrolbenzylamine). As the pinene was but slightly dextro-rotatory, the authors assume that they had to deal with a mixture of *d*- and *l*-α-pinene in which the dextro-rotatory variety predominated. The oil also contained borneol which was recognized by its oxidation to camphor (m. p. of the oxime 118 to 119°). Linalool may possibly form part of the oil too. The fraction to be considered in respect of this alcohol yielded a body smelling like citral, after oxidation with chromic acid, but it was not possible to obtain a citral derivative in a pure state.

Borneol is undoubtedly present, partly as ester. Of combined acids the presence of formic and acetic acids was proved by their silver salts.

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[1]) *Journ. chem. Soc.* **105** (1914), 2613; *Chem. Zentralbl.* **1915**, I. 200. — [2]) *Berichte von Roure-Bertrand Fils* April **1914**, 9. — [3]) *Pharmaceutical Journ.* III. **10** (1879), 102. — [4]) *Journ. Americ. chem. Soc.* **36** (1914) 2182.

Camphor Oil. In 1913 the camphor exports from the Chinese province of Fukien amounted altogether to 210 piculs (12694,5 kilos) whereof 207 piculs came from Foochow and 3 piculs from Amoy. Compared with 1912 these exports are about 1900 kilos higher, but they are still far behind the average attained in former years[1]).

According to an American contemporary[2]) the Bureau of Forestry of the Philippine Government, after practical experiments extending over two years, contemplates the cultivation of camphor trees on a large scale. For this purpose the Philippine archipelago offers a sufficiency of suitable soil.

Cananga Oil. Several samples submitted to us recently showed a higher ester value (38,2 to 42,9) than normal cananga oils, and were also of insufficient solubility, thus rendering them suspicious of having been adulterated with a fixed oil. After distillation with steam their ester value went back to the normal figure (10 to 35), the oils becoming clearly soluble in 1 volume of 95 p. c. alcohol; on diluting up to 10 volumes only slight turbidity showed itself, whereas the oils in their original state, though of the same initial solubility, separated globules of oil on being diluted up to 10 volumes of 95 p. c. alcohol. Moreover, divergences were observed in the amount, as well as in ester value, of the residues obtained in the process of steam rectification. Two pure oils, examined at the same time for comparison purposes, yielded distillation residues of 2,6 and 2,8 p. c. respectively, with an acid v. of 1,8 and an ester v. of 98,8 in one instance, and an acid v. of 5,6, and ester v. of 66,2 in the second instance. The distillation residues of the two suspected oils were from 6,5 to 8,7 p. c. and their sap. v. from 183 to 191; from which it may be deduced that they contained small quantities of a fixed oil. It could not be determined whether this was a case of intentional adulteration, or accidental impurity.

Cardamom Oil. E. M. Holmes[3]) gives the following constants for an oil distilled, with a yield of 1,2 p.c., from Korarima-cardamoms (*Amomum Korarima*, Pereira): $d_{15°}$ 0,9038; α_D — 3°; acid v. 3,6; ester v. 22,1; soluble in 1/2 volume of 90 p.c. alcohol. The odour differs from that of normal cardamom oil, which possibly explains Dymock's suggestion to call the Korarima cardamom "Nutmeg cardamom". According to Holmes, in Gildemeister and Hoffmann's book on essential oils, *Amomum angustifolium*, Sonn. is mentioned as mother-plant. We may point out that this only applies to the first edition, whereas the second edition of the work referred to correctly mentions *Amomum Korarima*, Pereira as being the mother-plant.

A picture of Korarima cardamoms is added to Holmes' treatise.

Cassia Oil. As is well known, Hirschsohn's lead acetate test[4]) is generally used, *i. a.*, to determine colophony in cassia oil. This test is carried out in the following manner. To a solution of one volume of oil in 3 volumes of 70 p.c. alcohol up to 1/2 volume of a freshly prepared saturated lead acetate solution in 70 p.c. alcohol is added drop by drop; precipitation will be observed if colophony be present.

According to an English contemporary[5]) this reaction may also be made use of for the quantitative determination of rosin. For this purpose 5 g. of oil are dissolved in 20 cc. of 70 p.c. alcohol to which 10 cc. (or more if necessary) of a saturated solution

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[1]) *Nachr. f. Hand., Ind. u. Landw.* 1914, No. 33, p. 7. — [2]) *Oil, Paint and Drug Reporter* **85** (1914), No. 11, p. 27. — [3]) *Perfum. Record* **5** (1914), 302. — [4]) *Pharm. Zeitschr. f. Russl.* **29** (1890), 255; *Report* October **1890**, p. 20, 21. — [5]) *Perfum. Record* **5** (1914), 264.

of lead acetate are added. The precipitate is collected on a tared Gooch filter (packed with ignited asbestos), thoroughly washed with 70 p.c. alcohol, and dried at 100° until constant weight is attained. The filtrate should be tested with more of the lead acetate solution and any further precipitate filtered off.

In this way an oil mixed with 10 p.c. of rosin gave 10,6 p.c. precipitate; one containing 15 p.c. gave 15,2 p.c., and one with 20 p.c. showed 19,7 p.c. of precipitate. Two pure cassia oils, containing 92 and 88 p.c. of aldehyde respectively, and acid values of 6 and 13, yielded no precipitate with lead acetate. Three other oils gave 10,1, 10,6 and 10,1 p.c., respectively. In these latter oils the aldehyde percentages were 82, 72, and 73 p.c., respectively, acid v. being 27, 23 and 29. These latter figures cannot be relied upon in the quantitative determination of added rosin, because the oils themselves contain varying quantities of cinnamic acid; the acid values do not, therefore, permit of any direct conclusions concerning the quantities of rosin present in the oil[1]).

The author of above article believes that his observations justify the conclusion that about 10 p.c. of rosin are systematically added to cassia oil in certain parts of the country of origin.

Oil of Cathetus fasciculata. On page 102 of our *Report* April **1914** we had given a description — under "Novelties" — of the oil of *Cathetus fasciculata,* Lour. *(Euphorbiaceae).* At the very same time a description also appeared in the *Report* of Roure-Bertrand Fils[2]). According to Roure-Bertrand Fils the mother-plant is a shrub about 3 feet high, with twigs pointing upward, with entire, flat and glabrous leaves; the flowers are small, axillary or singly arranged. According to Murat the shrub is in full florescence in the month of August. Distillation begins towards the end of January and yields varying results, according to soil and according to whether fresh or dried plants are used. Consequently the oil is sometimes of a green, sometimes of a yellow colour. Differences in soil may possibly account for these differences in colour. The properties of green as well as of yellow oils observed by Roure-Bertrand Fils, as well as our own observations, are collected in the table below. The oil contained 31 p.c. of cineol (resorcinol method).

	Oil		
	green	yellow	Schimmel & Co.
d_{150}	0,8871	0,8862	0,8897
α_D	— 4° 40′	— 1° 22′	— 4° 34′
acid v.	4,2	0,7	1,9
ester v.	4,2	3,5	3,7
ester value after acetylation	42,0	49,5	44,8
soluble in	4,5 volumes and more of 85 p.c. alcohol.	3 volumes	—

Oil of Chamaecyparis Lawsoniana. Of the "Port Orford cedar" *(Chamaecyparis Lawsoniana,* Parl., N.O. *Pinaceae)* only the oil of the leaves had been prepared so far[3]).

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[1]) In the above article it is stated that C. F. Yates [*Perfum. Record* **3** (1912), 83] recommended the acid value being made use of in the determination of colophony in cassia oil. To obviate misunderstandings we may say this was done first by H. Gilbert [*Chem. Ztg.* **13** (1889), 1406] who laid special stress on the usefulness of the acid value in the quantitative determination of the rosin. In the course of the years we have repeatedly pointed out how acid value in cassia oil is increased by colophony. — [2]) *Berichte von Roure-Bertrand Fils* April **1914**, 5. — [3]) *Report* October **1910**, 144, 145.

The oil from the wood shows utterly different properties about which A. W. Schorger[1]) has published a report. This oil possesses a strong and pleasant odour, but appears to irritate the kidneys, for which reason the saw-mills cannot cut the wood uninterruptedly for any length of time, lest the workmen should become affected by the oil vapours. The oil examined by Schorger had been distilled 4 years previously from selected, very resinous pieces of wood. It had been obtained by steam distillation, the yield being about 10 p.c. and at the time of distillation the constants were as follows: $d_{15°}$ 0,891; $n_{D15°}$ 1,477; it had the above-mentioned physiological effect. A red residue was left in the still. After 4 years the constants were as follows: $d_{15°}$ 0,9061; $n_{D15°}$ 1,4806. Schorger shook the oil with a soda solution and distilled it with steam over soda, in which process 16,4 p.c. by volume were left in the residue. The oil thus obtained did not seem to affect the kidneys any longer, neither did it leave a red distillation residue. The rectified oil had the following properties: $d_{15°}$ 0,8905; $\alpha_{D25°}$ + 39,6°; $n_{D15°}$ 1,4758; acid v. 0,3; ester v. 32,8; ester v. after acetylation 71,57. 60,5 p.c. boiled from 155 to 157°, 3 p.c. from 157 to 170°, 4 p.c. from 170 to 180°, 20,5 p.c. from 100 to 130° (15 mm.), 7 p.c. from 130 to 160° (15 mm.) and 1 p.c. from 160 to 190° (15 mm). When distilled under ordinary pressure, the oil begins to decompose at 180°. The presence of the following constituents has been proved: 60 to 61 p.c. *d*-α-pinene ($[\alpha]_D$ + 51,52°, the highest rotation observed in pinene so far). The pinene was oxidized to *d*-pinonic acid of the m. p. 68 to 69°; $[\alpha]_D$ + 92,69°; semicarbazone of pinonic acid, m. p. 203 to 205°. The oil also contained 6 to 7 p.c. of dipentene (tetrabromide, m. p. 124°), 11 p.c. of free *l*-borneol (constants; oxidation to camphor), 6 to 7 p.c. of cadinene (dihydrochloride, m. p. 117 to 118°), free formic and acetic acids (silver salts) and combined formic and caprinic acids (silver salts). Borneol is probably present in the oil, esterified with formic, acetic and caprinic acids. In the resinified oil free formic, acetic and caprinic acids are present.

Cinnamon Oil. H. A. Phillips[2]) has examined the stability of free cinnamic aldehyde, as well as of the aldehyde occurring in cinnamon oil. He allowed cinnamic aldehyde to stand in an uncovered dish in the air, and found that acidity increased about 1 p.c. per day; with cinnamon oil, however, the increase only amounted to about 0,1 p.c. per day.

Cinnamic aldehyde, containing 98,5 p.c. of aldehyde (after Hanuš' method) and 2,3 p.c. of acid, showed 97 p.c. of aldehyde and 3,3 p.c. of acid after distillation by steam. Cinnamon oil contained 86,5 p.c. of aldehyde and 2,3 p.c. of acid before distillation, and 85 p.c. aldehyde and 1,2 p.c. of acid after distillation. When distilling a mixture of cinnamic aldehyde or cinnamon oil with water, the distillation lasting from 6 to 8 hours, it was found that practically no increase in the acid value had taken place.

It is evident, from these experiments, that cinnamic aldehyde, upon distillation with steam, as well as in the course of distillation of cinnamon oil, hardly oxidizes at all.

In reference to the cinnamic aldehyde of cassia oil we observed a number of years ago[3]) that the other constituents present in this oil protect the aldehyde against oxidation.

Citronella Oil. According to an English contemporary[4]) Java citronella oils of a fishy odour have been examined in England, and have been found to contain far

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[1]) *Journ. Ind. Eng. Chemistry* **6** (1914), 631. — [2]) *Pharmaceutical Journ.* **93** (1914), 129. — *Chemist and Druggist* **85** (1914), 172. — [3]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II. — [4]) *Perfum. Record* **5** (1914), 276.

more geraniol than citronellal. Whereas with high-class Java oils, containing 92 to 94 p. c. of so-called total geraniol, geraniol proper amounted to about 50 p. c. and citronellal to perhaps 44 p. c., these inferior oils showed only 79,5 to 82,5 p. c. of so-called total geraniol, whereof about 50 to 58 p. c. was geraniol proper and from 22 to 32 p. c. citronellal; moreover, the specific gravity of these oils was higher (0,899 to 0,901) than in the case of good oils (0,884 to 0,897)[1]). The author of the article in question seems to be in some doubt as to the causes of this anomaly. He seems to think that it might possibly be due to some Ceylon citronella oil having been added to the Java oil; or to the raw material, the grass used having perhaps been some hybridized plant, closely related to the Ceylon variety, or that some differences in the cultivation reacted on the quality of the grass; he also touches upon the possibility of overheating in the course of distillation. His observations lead him to the conclusion that, apart from the total geraniol percentage, it would be advisable to value the oil also according to its percentage of citronellal, by establishing a mininum limit for this latter body.

To obviate misunderstandings we would add that the geraniol percentage was ascertained according to the method of Dupont and Labaune. In our *Report* on this method[2]) we had pointed out that not only the geraniol but all the alcohols present in the oil, either free or in the form of ester, are ascertained thereby, thus offering more especially indications as to the quantity of citronellal, which can be deduced from the difference between the so-called total geraniol and the alcoholic parts. For the test of geraniol proper the only suitable process is our phthalic anhydride test[3]). As mentioned in our previous *Report* (page 44) by means of this test we found from 26 to 44,4 p. c. of geraniol in Java citronella oils. The citronellal percentage, as established by Dupont and Labaune's method, amounted to 23,4 to from 50,1 p. c. We stated at the time that oils with a high citronellal percentage were almost invariably of especially fine odour, and of a low specific gravity.

Of oxides of the terpene group, represented in essential oils, only cineol, $C_{10}H_{16}O$, and calameone, $C_{15}H_{26}O_2$, were known so far, whereas carlina oxide, $C_{13}H_{10}O$, must probably be looked upon as a phenyl-1-α-furyl-3-allene. A body, $C_{20}H_{34}O$, which was proved by K. E. Spornitz[4]) in the high-boiling (b. p. 190 to 200° at 15 mm.) parts of Java citronella oil and which was called dicitronella oxide, is to be considered as an oxide of the diterpene group. It was distilled over sodium, yielding a colourless liquid which boiled from 182 to 183° (12 mm.): $d_{20°}^{20°}$ 0,9199; α_D — 4°; n_D 1,49179; mol. refr. found 91,43, calculated for $C_{20}H_{34}O/\bar{2}$ 90,85. When boiled with acetic anhydride and sodium acetate this body formed no ester, neither did it split off water with concentrated formic acid, nor change when treated with sodium and alcohol. Elementary analysis as well as determination of molecular weight in benzene solution, after Beckmann, agreed with the formula $C_{20}H_{34}O$. By the introduction under pressure, in the presence of platinum black, of hydrogen into the ethereal solution or into the glacial acetic solution, dicitronella oxide may easily be reduced to tetrahydrodicitronella oxide, $C_{20}H_{38}O$; b. p. 180 to 185° (11,5 mm.); $d_{20°}^{20°}$ 0,9001; n_D 1,47457. By introducing dried hydrochloric acid gas into the ethereal solution of dicitronella oxide, a monohydrochloride, m. p. 107,5°,

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[1]) The rotation of the inferior oils is given as —1 to —2°, of the normal oils as +1°. This might lead to the belief, that dextro-rotation is a characteristic of Java citronella oils. This is not the case; on the contrary Java citronella oils are mostly laevo-rotatory (generally not exceeding —3°), whereas dextro-rotation is the exception, and not the rule. See Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 241. — [2]) *Report* October **1912**, 40. — [3]) *Ibidem* 43. — [4]) *Berl. Berichte* **47** (1914), 2478.

was obtained. When boiled with alcoholic potash lye, the hydrochloride was converted into an oxide $C_{20}H_{34}O$, which the author calls *iso*dicitronella oxide. It contains one double linkage less than the original oxide. B. p. 176 to 180° (11 mm.); $d_{20°}^{20°}$ 0,9518; n_D 1,49692; molecular refraction found 89,14, calculated for $C_{20}H_{34}O/\overline{1}$ 88,98. The double linkage could be saturated by heating with sodium and alcohol, resulting in dihydro-*iso*dicitronella oxide, m. p. 71°. When dicitronella oxide was ozonized, chiefly neutral bodies were obtained after the decomposition of the ozonide.

The oxide $C_{20}H_{34}O$ mentioned on page 85, which Semmler and Jonas prepared by heating citronellal with anhydrous oxalic acid, is closely related to dicitronella oxide, but it differs from it inasmuch as it does not yield a solid hydrochloride and that the hydrogenation product is optically active, whereas the hydrogenation product of the natural body has no rotatory power.

Clove Oil. In its *Bulletin* of April/June **1914**[1]), the Imperial Institute in London describes several distillates obtained from cloves and clove leaves in the island of Mauritius. The properties of these oils, which agree approximately with those found in London, have already been reported upon in our last *Report* (page 47), as the Imperial Institute had sent us samples of the oils. We may here add that in both cases the yield was small, *viz.*, 10,2 and 11,5 p. c. with cloves, and 1,62 p. c. with clove leaves.

Cochlearia (Spoonwort) Oil. For spoonwort oil, obtained to the extent of 0,007 p. c. from crushed herb, Th. A. van Pienbroek and J. Pinkhof[2]) give the following values: $d_{15°}$ 0,959; $[\alpha]_D$ +70,4° (3 p. c. solution in 90 p. c. alcohol); $n_{D20°}$ 1,4914; soluble in 1,9 volume of 90 p. c. alcohol; not clearly soluble in 80 p. c. alcohol. The oil contained 94 p. c. of butyl mustard oil, determined with ammonia and nitrate of silver.

When freshly distilled, the oil was yellow, but it soon became darker little by little, when in contact with the air.

About the oil from *Cochlearia danica*, L., see page 79 of this *Report*.

An experimental cultivation of spoonwort in Austria is dealt with on page 64 of this *Report*.

Copaiba Balsam Oil. On page 48 of our *Report* April **1914** we stated that in oil of African copaiba balsam a laevo-rotatory sesquiterpene was present, which differed materially from cadinene in its physical properties, but which nevertheless yielded cadinene hydrochloride. This sesquiterpene has been examined more closely by F. W. Semmler and H. Stenzel[3]) and has been called copaene. Purified by repeated distillation the sesquiterpene, upon combustion, furnished values agreeing with the formula $C_{15}H_{24}$. By reduction with platinum and hydrogen in absolute ethereal solution it formed dihydrocopaene, $C_{15}H_{26}$ (b. p. 118 to 121° at 12 mm.); oxidation with ozone led to a very viscid acid, the copaene ketonic acid, the silver salt of which was analysed. It had the formula $C_{15}H_{24}O_3$ and formed a methyl ester of the b. p. 182 to 185° (14 mm.). When oxidized with permanganate of potash in aqueous acetone, copaene also yielded copaene ketonic acid; this acid is so strongly viscid that its physical values could not be determined. Being a ketonic acid it forms a semicarbazone melting at 221°;

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[1]) *Bull. Imp. Inst.* **12** (1914), 232. — [2]) *Pharm. Weekblad* **51** (1914), 995. From a special reprint kindly sent to us. — [3]) *Berl. Berichte* **47** (1914), 2555.

the semicarbazone of the copaene ketonic acid methylester melted at 193,5 to 194°. Oxidation of the copaene ketonic acid with alkaline bromine solution led to a dicarboxylic acid $C_{12}H_{18}O_4$, copaene dicarboxylic acid, the methyl ester of which boiled at 178 to 182° (14 mm.).

The authors presume that, judging from its chemical nature, copaene belongs to a new type of tricyclic sesquiterpenes, as by the addition of hydrogen chloride it readily passes into the type of cadinene. The latter is bicyclic and is probably based on a hydrogenated naphthalene nucleus.

J. D. Riedel, Berlin[1]), describes a balsam of copaiba originating from Manaos, the capital of the Brazilian province of Amazonas. $d_{15°}$ 0,930; α_D — 40°; acid v. 23,8; sap. v. 42,1. This balsam yielded about 80 p. c. of an oil which rotated α_D — 35° 20′ The optical rotation of the resin left after distillation, determined in chloroform solution, was about — 55°, calculated on pure resin in 100 mm. thickness.

At the same time Riedel examined several other balsams of copaiba of different origin. Maracaibo balsams rotated from + 24 to + 30°, the oils obtained therefrom showed — 6 to — 13°, and the resinous distillation-residue (about 65 p.c.) showed + 40 to + 60°. A sample of Maturin balsam showed a rotation of α_D + 35°, the corresponding oil α_D — 9°, and the residual resin (about 57 p.c.) about + 70°. African balsam showed α_D + 1°20′, the oil obtained from it α_D + 27° 20′ and the residual resin (about 51 p.c.) about — 23°.

We too had occasion to examine Manaos balsams several times of late. One sample showed the following constants: $d_{15°}$ 0,9280; α_D — 29° 30′; $n_{D20°}$ 1,50457; acid v. 23,2; ester v. 5,5; the oil drawn from it (yield about 81 p.c.) $d_{15°}$ 0,9036; α_D — 32° 28′; $n_{D20°}$ 1,50092; acid v. 0,6; ester v. 6,4. Two further distillates of Manaos balsams had the following properties: $d_{15°}$ 0,9068 and 0,9095; α_D — 16° 4′ and — 30° 6′; $n_{D20°}$ 1,50045 and 1,53012; acid v. of both 0,3; ester v. 3,7 and 0,9, both soluble in 6 volumes and more of 95 p. c. alcohol. The yield of oil was 83,4 p.c. in one instance, and 79,6 p. c. in the other.

Costus root Oil. F. W. Semmler and J. Feldstein[2]) report on the examination of a costus root oil supplied by ourselves, for which they established the following figures: b. p. 60 to 215° (11 mm.); $d^{20°}_{16°}$ 0,9851; α_D + 15° 24′; n_D 1,51264. In a fraction of the b. p. 200 to 210° (11 mm.) ($d_{21°}$ 1,0749; α_D + 38°; n_D 1,53103) a lactone $C_{15}H_{20}O_2$ was proved, which, for purification, was converted into the corresponding hydroxy acid, the methyl ester of which reconverted into the lactone on boiling. The authors call the body costolactone. It boiled at 205 to 211° (13 mm.); $d_{21°}$ 1,0891; α_D + 28°; n_D 1,53043; molecular refraction calculated for $C_{15}H_{20}O_2/\bar{=}_2$ 65,91, found 65,85. Costolactone is bicyclic and diolefinic.

A fraction of the b. p. 190 to 200° (11 mm.) ($d_{21°}$ 1,0501; α_D + 44°; n_D 1,52703) contained a diolefinic bicyclic acid $C_{15}H_{22}O_2$, *i. e.* costic acid, which after purification over its silver salt showed the following properties: b. p. 200 to 205° (11 mm.); $d_{21°}$ 1,0508; α_D + 40°; n_D 1,51912; molecular refraction calculated for $C_{15}H_{22}O_2/\bar{=}_2$ 67,85, found 67,73. The methyl ester boiled at 170 to 175° (11 mm.).

The same fraction contained a lactone $C_{15}H_{22}O_2$, which the authors call dihydrocostolactone. The silver salt of the corresponding hydroxy-acid was converted into its methyl ester which, upon distillation *in vacuo*, returned dihydrocostolactone. Thus purified it showed: b. p. 210 to 213° (19 mm.); $d_{22°}$ 1,0776; α_D + 48°; n_D 1,52289;

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[1]) *Riedels Berichte und Mentor*, **1914**, 27. — [2]) *Berl. Berichte* **47** (1914), 2433, 2687.

molecular refraction calculated for $C_{15}H_{22}O_2$/= 66,31, found 66,31. The dihydrocostolactone may be prepared from costic acid by heating with sulphuric acid of 33 p. c. Upon hydrogenation with platinum and hydrogen, costolactone as well as dihydrocostolactone are converted into the same tetrahydrocostolactone $C_{15}H_{24}O_2$ of the b. p. 198 to 202° (13 mm.); $d_{21°}$ 1,0451; $\alpha_D + 33°$; n_D 1,50510; molecular refraction calculated for $C_{15}H_{24}O_2$ 66,71, found 66,99. Costolactone, dihydrocostolactone and costic acid are therefore in genetical correlation, firstly because costic acid may be converted into dihydrocostolactone, and secondly costolactone and dihydrocostolactone into the above-mentioned tetrahydrocostolactone. Most likely they belong to the bicyclic terpene type of the sesquiterpene class. Costolactone is an isomeride of alantolactone.

Another fraction (b. p. 175 to 190° at 11 mm.; $d_{21°}$ 1,0082; $\alpha_D + 33°$; n_D 1,51962) contained a doubly unsaturated, bicyclic primary sesquiterpene alcohol $C_{15}H_{24}O$, for which the authors suggest the name of costol. It reacts readily with phthalic anhydride, and, recovered from the hydrogen phthalate, it boiled at 169 to 171° (11 mm.); $d_{21°}$ 0,9830; $\alpha_D + 13°$; n_D 1,52000; molecular refraction calculated for $C_{15}H_{24}O$/$\bar{2}$ 67,67, found 67,9. By oxidation with chromic acid in glacial acetic solution, costol may be converted into an aldehyde which is characterized by a semicarbazone of the m. p. 217 to 218°. Theoretically the aldehyde ought to show a density of about 0,99, but in reality it has a specific gravity of 0,9541 at 22° (b. p. 164 to 165° at 15 mm.; $\alpha_D + 24°$; n_D 1,50645); proving that in the course of oxidation transposition must have taken place. With phosphorus pentachloride, costol produced costyl chloride, $C_{15}H_{23}Cl$ of a b. p. of 160 to 165° at 13 mm., from which, by reduction with sodium and alcohol, the sesquiterpene *iso*costene was obtained: b. p. 130 to 135° (12 mm.); $d_{21°}$ 0,9062; $\alpha_D + 31°$; n_D 1,50246; molecular refraction calculated for $C_{15}H_{24}$/$\bar{2}$ 66,15, found 66,37. *Iso*costene appears to be a diolefinic sesquiterpene of the caryophyllene type. Costol was obtained by reducing the costus acid methyl ester with sodium and alcohol.

In a fraction boiling at 160 to 175° (11 mm.) ($d_{21°}$ 0,9235; $\alpha_D + 14°$; n_D 1,49994) a hydrocarbon $C_{17}H_{28}$ (?) was present, which was given the name of aplotaxene. It boiled from 154 to 156° (11 mm.) and showed the low specific gravity of 0,8604 (21°). It was not possible, however, to obtain it quite free from oxygenous admixtures. By reduction with sodium and alcohol it furnished dihydroaplotaxene $C_{17}H_{30}$ (b. p. 154 to 157°; $d_{21°}$ 0,8177) which, by means of hydrogen and platinum black, was converted into octohydroaplotaxene (b. p. 159 to 163° at 11 mm.; $d^{21°}_{16°}$ 0,7805). This body is certainly identical with *n*-heptadecane. It follows that aplotaxene is an aliphatic hydrocarbon with normal chain, containing four double linkings, two of which are in conjugated position. The costus oil fractions of the b. p. 100 to 130° (11 mm.) and 130 to 150° (11 mm.) contained two sesquiterpenes which were designated α- and β-costene.

α-Costene boils from 122 to 126° (12 mm.); $d_{21°}$ 0,9014; $\alpha_D - 12°$; n_D 1,49807; molecular refraction calculated for $C_{15}H_{24}$/$\bar{2}$ 66,15, found 66,37. In the process of hydration after Bertram and Walbaum an alcohol was formed of the b. p. 150 to 165° (14,5 mm.).

β-Costene boiled from 144 to 149° (18 mm.); $d_{22°}$ 0,8728; $\alpha_D + 6°$; n_D 1,4905; molecular refraction calculated for $C_{15}H_{24}$/$\bar{3}$ 67,86, found 67,65.

Finally a fraction of the b. p. 60 to 100° (11 mm.) was examined. It contained phellandrene (bisnitrosite, m. p. 106 to 108°), camphene (conversion into *iso*borneol) and probably a terpene alcohol $C_{10}H_{16}O$.

Expressed by percentage the composition of costus oil may be approximately given as follows: —

About 0,4 p.c. of camphene; 0,4 p.c. phellandrene; 0,2 p.c. terpene alcohol; 6 p.c. α-costene; 6 p.c. β-costene; 20 p.c. aplotaxene; 7 p.c. costol; 15 p.c. dihydrocostolactone; 11 p.c. costolactone, and 14 p.c. costic acid.

Cubeb Oil. For the new British Pharmacopoeia, C. A. Hill and J. C. Umney[1]) had made the suggestion that at least 80 p.c. of cubeb oil should pass over between 250 and 280°.

From more recent observations, however, which Umney made in collaboration with E. T. Brewis[2]), it was found that this requirement could not be upheld. In their opinion it is sufficient if 60 to 65 p.c. of the oil are required to pass over within the limits of temperature indicated. Unfortunately, once again an important point is not touched upon at all, *viz.*, the character of the distilling flask.

At the same time the two authors give the properties of 7 cubeb oils produced in the factory of Stafford Allen & Sons, Ltd. With six of the oils the values observed were found to be within the following figures: $d_{25°}$ 0,919 to 0,924; α_D — 27,2 to — 29,4°; $n_{D25°}$ 1,4928 to 1,4950; in the course of distillation 14 to 32 p.c. passed over below 250°, and 64 to 80 p.c. between 250 and 280°. The seventh oil differed a little in its density and boiling point: $d_{25°}$ 0,927; α_D — 27,2°; $n_{D25°}$ 1,4950; 50 p.c. passed over below 250°, and 44 p.c. between 250 and 280°.

Oil of Daniella thurifera. From the resin of *Daniella thurifera*, Benn. (N. O. *Leguminosae*)[3]) originating from Togo, W. Lenz[4]) obtained 23 p.c. of an oil which contained no phenols, and only traces of aldehydic constituents. 52 p.c. of the oil boiled from 120 to 290°. On passing in hydrogen chloride, the fractions of a b. p. 259 to 270° ($d_{20°}$ 0,9850; α_D 67,83° [+ ?]) yielded cadinene hydrochloride (m. p. 119°; $[\alpha]_D$ — 39,82°), from which the author infers the presence of cadinene in the original oil. The oil also contained a bluish green high-boiling fraction of the density 0,9845 (20°); α_D 5,98° (+ ?).

From a sample of the balsam placed at our disposal by the author some considerable time back, we obtained upon distillation with steam 58 p.c. of a colourless oil of the following constants: $d_{15°}$ 0,9216; α_D — 5° 43′; $n_{D20°}$ 1,50670; acid v. 0; ester v. 1,9; turbidly soluble in 10 volumes of 95 p.c. alcohol. Under a pressure of 3 to 4 mm. 74 p.c. of the oil passed over between 95 and 108°, whereas under atmospheric pressure it began to boil at 268°, but in the latter case distillation could not be carried through in consequence of decomposition, water being split off. Under the influence of hydrogen chloride gas we also obtained considerable amounts of cadinene dihydrochloride, m. p. 118°.

Oil of Daviesia latifolia. According to F. B. Power and A. H. Salway[5]), the leaves and twigs of the Australian leguminosa *Daviesia latifolia*, R. Br. contain traces of a volatile oil in which benzoic acid (m. p. 121°) is present. After elimination of the benzoic acid the oil boiled from 200 to 220°.

Elecampane Oil. The properties of an elecampane oil of our own drawing were communicated in our *Report* of April **1912**, page 61. It was a distillate showing a full percentage of alantolactone, being a solid mass in consequence. Lately we again had an opportunity of analysing two distillates of our own manufacture the alantol-

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[1]) *Chemist and Druggist* **76** (1910), 271; *Report* April **1910**, 135. — [2]) *Perfum. Record* **5** (1910), 256. — [3]) Comp. *Report* April **1911**, 145. — [4]) *Berl. Berichte* **47** (1914), 1989. — [5]) *Journ. chem. Soc.* **105** (1914), 767.

actone of which, however, had been removed in part. These oils had not, therefore, the characteristics of the above-mentioned oil, but were viscid, of a dark brown colour and of a peculiar odour. They shewed the following values: $d_{15°}$ 1,0407 and 1,0430; $n_{D20°}$ 1,52324 and 1,52245; acid v. 14,9 and 10,9; ester v. 155,6 and 167,3; ester v. after acetylation, ascertained with one of the oils only, 181,6. Both oils gave a clear solution in 95 p.c. alcohol, up to about 1 vol., but became turbid on further dilution, one of the solutions showing a deposit after prolonged standing. The first-named distillate behaved similarly in 90 p.c. alcohol; the second, however, showed a slight precipitation from the beginning.

Oil of Elsholtzia cristata. Y. Asahina and Y. Murayama[1]) describe the oil of *Elsholtzia cristata*, Willd., a labiata which was formerly used as an antipyretic and a diuretic in Japan, but which now belongs to the list of obsolete medicaments. The dried herb yielded 2 p.c. of a yellow volatile oil, a mobile liquid becoming brown by degrees, and of a peculiar odour. $d_{15°}$ 0,970; α_D — 2,7°; acid v. 0; sap. v. 1,8; sap. v. after acetylation 14,7. It boiled chiefly between 210 and 215°. On shaking with caustic potash or bisulphite liquor but very little of the oil was dissolved; when heated with hydrogen iodide no methyl iodide was split off. With semicarbazide hydrochloride the oil yielded a semicarbazone of a m. p. 171°, with hydroxylamine hydrochloride an oxime melting at 54°; the ketone regenerated from these derivatives was an almost colourless, very mobile oil of a peculiar aromatic odour: b. p. 87 to 88° (10 mm.); 112° (31 mm.); 210° (764 mm.); $d_{20°}$ 0,9817; $\alpha_D \pm 0$; $n_{D20°}$ 1,48424. The authors call the ketone elsholtzione; it has the empirical composition $C_{10}H_{14}O_2$. When reduced with amalgamated zinc and hydrochloric acid, after Clemmensen[2]), it yielded a small quantity of a body $C_{10}H_{16}O$, which does not form a semicarbazone. Oxidation with potassium permanganate led to *iso*valeric acid, which was characterized by the analysis of the silver salt and conversion into *iso*valeranilide (m. p. 115°). Under the influence of amylnitrite and sodium on the elsholtzione, elsholtzic acid $C_6H_6O_3$, m. p. 134° was obtained. In elsholtzione we have probably to deal with a furan derivative, possibly of the formula $C_4H_2O\begin{matrix}CH_3\\ CO\cdot CH_2\cdot CH(CH_3)_2\end{matrix}$. In connection with this examination the authors produced some alkylfuryl ketones by synthesis.

Essential Oils, Sicilian and Calabrian.

In an article on the hybrids of the edible *Citrus* varieties, L. Trabut[3]) puts forth the suggestion that it will be necessary to produce new *Citrus* varieties by cross-fertilization. In his opinion numerous and valuable cultivation varieties might be obtained in this manner, and at the same time it might be possible by this means to ascertain the mother-plant of the present-day *Citrus* hybrids.

Bergamot Oil. How far, under certain conditions, "art" may go, is shewn by two samples of "artificial bergamot oil" which were submitted to us for analysis. The oils had the following constants:—

I. $d_{15°}$ 1,0432; α_D + 7° 30′; acid v. 0,3; ester v. 403,3
II. $d_{15°}$ 1,0858; α_D + 7° 30′; „ „ 0,9; „ „ 577,1.

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[1]) *Arch. der Pharm.* **252** (1914), 435. — [2]) Comp. *Report* April **1913**, 141. — [3]) *Journ. d'Agriculture tropicale* **14** (1914), 65.

Even for artificial oils, density and ester values are abnormal to such an extent that from them alone the peculiar composition of the oils may be judged. Based on the ester v., the ester, calculated for linalyl acetate, would be 141 p.c. and 202 p.c. respectively, figures which are quite impossible and from which it can be deduced at once that considerable quantities of esters are present which should not be found even in artificial oils. Further examination revealed the fact that in both samples these esters were not linalyl acetate, as should be the case in an artificial bergamot oil, but mostly bodies of no value for the odour, namely, phthalic acid esters in one sample (probably diethyl phthalate) and glyceryl acetate in the other. As both oils contained about 70 p.c. of these bodies respectively, the proof of their presence was easy, in spite of the smallness of the samples at our disposal. Glyceryl acetate was isolated by shaking out with a 5 p.c. solution of alcohol and was recognized *i. a.* by the high sap. value (676), whereas in the other oil the acid, which did not pass over with steam in the determination of the acid number II (*Report* October **1910**, p. 61), was identified as phthalic acid (m.p. 203°; m. p. of the anhydride obtained by sublimation 130°; fluorescein reaction).

As mentioned above, both samples contained about 70 p.c. of these esters, that is to say such an extent that one cannot speak of artificial bergamot oils any longer, but more correctly of cheap and — from the point of view of their strength — valueless esters which had been perfumed more or less cleverly so as to resemble bergamot oil. Such concoctions have, needless to say, nothing in common with a scientifically prepared artificial bergamot oil.

Lemon Oil. In our last *Report* (page 59) we communicated a process elaborated by E. Böcker for the determination of hydrocarbon percentage in concentrated lemon oils. For this purpose the oil is first freed from citral by means of sodium sulphite; thereupon the other aromatic bodies are shaken out with chilled alcohol of 51 p.c. strength. The remaining hydrocarbons are calculated by volume, the result is compared with the original oil and the percentage thus determined.

In continuing his studies on the valuation of concentrated lemon oils, Böcker[1]) has arrived at the result that a juxtaposition of the percentages of citral and hydrocarbons respectively permits of conclusions being drawn as to whether such oils are pure or adulterated with citral from lemongrass oil. Experiments with two oils, mixed with 20 p.c. of citral, however, showed that by this means only about half the amount of adulteration can be ascertained, but at all events the minimum of adulteration may be determined in this manner. On the same occasion it was once more proved by experiment that the citral percentage of concentrated oils is ascertained with greatest certainty by the neutral sodium sulphite method as indicated by Burgess.

In his valuation Böcker starts from the observation that a lemon oil, which has been completely freed from hydrocarbons, contains at most 66 p.c. of citral, from which deduction he establishes the following table:—

Hydrocarbons	Highest permissible citral percentage	Hydrocarbons	Highest permissible citral percentage
0 p.c.	66 p.c.	30 p.c.	46,2 p.c.
5 „	62,7 „	35 „	42,9 „
10 „	59,4 „	40 „	39,6 „
15 „	56,1 „	45 „	36,3 „
20 „	52,8 „	50 „	33 „
25 „	49,5 „		

[1]) *Journ. f. prakt. Chem.* II. **90** (1914), 393.

This table may be completed *ad lib.*, every additional 1 p.c. of hydrocarbon corresponding with 0,66 p.c. less citral percentage. Thus, when examining a concentrated lemon oil, a glance at above table shews whether the hydrocarbon percentage found in the oil is in accordance with the citral percentage. If the oil contains more citral than is permissible according to this table, it is a proof of adulteration with lemongrass citral. Based on the highest permissible citral percentage (table), corresponding to the ascertained amount of hydrocarbon, the minimum added quantity of foreign citral is found by calculating how much lemon oil citral should be contained at most in the oil under examination. This figure is deducted from the percentage of citral as established by the sulphite method. The difference indicates the minimum of adulteration.

From one of the examples adduced by Böcker, the manner of calculation is explained more clearly. If in a given oil 15 p.c. of hydrocarbons and 61 p.c. citral have been found, a reference to above table shows that these values are not in agreement, for in an oil containing 15 p.c. of hydrocarbons the citral percentage should not exceed 56 p.c. The oil must, therefore, have been mixed with foreign citral. As a normal oil, showing 56 p.c. citral, should contain $100 - 56 = 44$ p.c. of non-citral parts, and as the oil under examination contains only $100 - 61 = 39$ p.c. of non-citral parts, the citral normally corresponding with the latter is shewn by the following ratio: $44 : 56 :: 39 : x$; $x = 49{,}63$. This figure indicates the highest possible percentage of real lemon oil citral in an oil containig 39 p.c. of non-citral bodies. 61 p.c. having been found, there must have been an adulteration with at least $61 - 49{,}63 = 11{,}37$ p.c. of added foreign citral.

Whether this manner of valuation can safely be relied upon in a general way for concentrated oils prepared by different manufacturing methods would have to be ascertained first by special experiments. It must not be lost sight of that besides hydrocarbons other bodies may have been eliminated from the original oil, according to the process that may have been made use of. In our opinion it does not necessarily follow that a high citral percentage is the result of adulteration.

For the determination of citral in lemon oils and lemon extracts, L. D. Little[1]) has elaborated a new colorimetric method. As a reagent he uses amidol (diamidophenol dihydrochloride), which is useful inasmuch as it does not react with acetaldehyde. It is not necessary, therefore, to specially purify the ethyl alcohol used for the solution, though it is advisable to distil it over caustic potash before use. The process is similar to Chace's method[2]), but is simpler, as there is no necessity of heating any of the solutions; the work may be carried out at ordinary room temperature. All that is required is an amido solution (0,2 g. amidol in 100 cc. of 65 p.c. alcohol) and a solution of citral in 50 p.c. alcohol containing 0,001 g. of citral per cc. Of this latter, which serves for comparison purposes, exactly 2 cc. are placed in a colorimetric tube, 20 cc. of 65 p.c. alcohol and 15 cc. of amidol solution are added and the mixture brought to a total of 50 cc. by adding 65 p.c. alcohol.

In similar manner a small quantity is mixed with a solution of the lemon oil or extract to be tested. The mixture is well shaken and allowed to settle for about 5 or 10 minutes, when the maximum coloration has been reached. The colour shades are then compared and the percentage of citral computed therefrom. In case of need the experiment is repeated after 15 to 20 minutes. In the case of extracts a 50 p.c.

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[1]) *Americ. Perfumer* 9 (1914), 74. — [2]) Comp. *Report* April 1907, 116.

solution is prepared with 50 p.c. alcohol, whereas with oils 1 g. is dissolved in enough of 85 p.c. alcohol to produce a total volume of 40 cc. The solution must be well filtered. Exactly 2 cc. are used for analysis in both instances, same as with the citral solution. The colorimeter used in these tests is a modification of the one designed by Schreiner. For further particulars concerning its construction we refer to the original treatise which contains an illustration of the apparatus.

According to this process, Little found from 3,14 to 4,68 p.c. of citral in lemon oils.

According to J. W. Marden and V. Elliott[1]), the best way to obtain citral from lemon oil is to extract 1 vol. of the oil with 18 volumes of 50 p.c. alcohol. In this manner an oil showing a citral percentage of 3,61 p. c. yielded 90 p. c. If 45 p.c. alcohol is used, the result is less favourable. As regards the theoretical reasonings which led the authors to this method (application of the distribution coefficient) we must refer readers to the original paper.

The authors do not state the method by which the citral percentage of lemon oil was determined.

Mandarin Oil, Japanese. From Japan we received, early last year, three samples of mandarin oil of Japanese origin, which are reported upon below. As they were colourless, it was evident that these oils had not been obtained by pressure, as is the custom in Italy, but by distillation. Consequently they were devoid of the fine aroma of the Italian oils, but smelled chiefly of limonene and cannot, therefore, compete with genuine mandarin oils. The different method of production is also illustrated by the chemical constants, as specified in the table below: —

	$d_{15°}$	α_D	α_D of the first 10 p.c. of the distillate	acid v.	ester v.	solubility in 90 p.c. alcohol
I.	0,8489;	$+92°35'$;	$+91°32'$;	0,3;	3,7;	5,5 vol. and more
II.	0,8528;	$+73°36'$;	$+66°10'$;	0,3;	3,6;	5,5 „ „ „
III.	0,8541;	$+68°5'$;	$+60°48'$;	0,3;	4,6;	5 „ „ „

Three oils sent us under the name of Mikan oil were evidently also mandarin oils, for the mandarin fruit is called *"Mikan"*[2]) in Japan. These oils showed somewhat similar constants to the above-mentioned distillates: —

$d_{15°}$ 0,8483; $\alpha_D + 92°20'$; soluble in 6 volumes and more of 90 p.c. alcohol
$d_{15°}$ 0,8478; $\alpha_D + 90°56'$; „ „ 6,2 „ „ „ „ 90 „ „
$d_{15°}$ 0,849; $\alpha_D + 90°35'$; „ „ abt. 10 „ „ „ „ 90 „ „

The values of Italian mandarin oil are within the following figures: $d_{15°}$ 0,854 to 0,859; $\alpha_D + 65$ to $+75°$; α_D of the first 10 p.c. of the distillate very little lower, or even up to 2° higher than the original oil; acid v. up to 1,7; ester v. 5 to 11; more or less turbidity when dissolved in 7 to 10 volumes of 90 p.c. alcohol.

An English journal[3]) also reports on a mandarin oil of Japanese origin. This oil too had been obtained by distillation and according to our contemporary it was of a very fine odour; it showed a specific gravity of 0,848 and a rotation of $+94°$. A slight fluorescence noticed in this oil is put down by the author to the presence of methyl ester of anthranilic acid. We may be permitted to point out that, according to

[1]) *Journ. Ind. Eng. Chemistry* **6** (1914), 930. — [2]) J. J. Rein, *Japan nach Reisen und Studien*, vol. II, p. 105, Leipzig 1886. — [3]) *Perfum. Record* **5** (1914), 72.

our observations, this latter body is not present in mandarin oil, but the methyl ester of methylanthranilic acid, which may well be the cause of the fluorescence observed in the oil in question.

Orange Oil, bitter, Chinese. According to P. Fenaroli[1]), the bitter Orange of Chinese origin (*Citrus sinensis*, Pers.) has for some time been made use of for the production of oil in Italy; he is of opinion, that it may become an important article of commerce in future. The odour resembles ordinary lemon oil, but has a hardly pleasant by-odour the elimination of which may possibly be attained in time. Fenaroli[3]) gives the following figures for this oil: $d_{15°}$ 0,847 to 0,848; $\alpha_{D20°}$ + 94,10 to + 95,40°; $n_{D17°}$ 1,47388 to 1,47408; not readily soluble in 80 p.c. alcohol. Soluble in 4 to 4 1/2 volumes of 90 p.c. alcohol. It boils at 80 mm. from 102 to 120° and contains 97 to 98 p.c. of *d*-limonene, besides small quantities of *d*-pinene (?), as well as some bodies boiling above 176°. Citral could not be found.

Orange Oil, West Indian. The *Journal of the Jamaica Agricultural Society*[2]) reports that before the great Messina earthquake West Indian orange oil was hardly to be found in the London market. After this catastrophe, however, more care was bestowed in Jamaica on the orange oil production which labours under some difficulties, inasmuch as the trees occur but singly, and not in groves, making the gathering of the fruit more difficult. Armed with hand-presses and bottles the farmers proceed from tree to tree, to collect the fruit and to peel it on the spot. The bottles are filled with a mixture of oil, vegetable slime and juice. When settled, the oil is poured off into copper vessels and exported to London. As the demand is but limited, steps are contemplated to avoid overproduction if possible.

On the properties of orange oils produced in Jamaica we gave some particulars on page 65 of our *Report* of October **1909**, which may now be completed, as we have examined several oils of the same origin in our laboratories since then. We have observed the following limits: —

Sweet orange Oil. $d_{15°}$ 0,8481 to 0,8491; $\alpha_{D20°}$ + 97° 43′ to + 98° 3′; α_D of the first 10 p.c. of the distillate + 96° 14′ to + 97° 30′, in every instance a little lower than the original oil; $n_{D20°}$ 1,46984 (1 test only); evaporation residue 1,4 to 2,0 p.c. In three aldehyde determinations carried out with phenylhydrazin[3]), 2,3, 2,7 and 3,8 p.c. respectively were found, calculated for decylic aldehyde.

Bitter orange Oil. $d_{15°}$ 0,8517 to 0,8537; $\alpha_{D20°}$ + 92° 57′ to + 96° 58′; α_D of the first 10 p.c. of the distillate + 92° 20′ to + 96° 40′, only in one instance higher than the original rotation; $n_{D20°}$ 1,47171 (1 test only); evaporation residue 2,6 to 3,2 p.c. Aldehyde content 0,75 to 1,5 p.c., calculated for decylic aldehyde.

Two further orange oils, also originating from the West Indies[4]), were submitted to us by the Imperial Institute of London. Both had been obtained by pressure, one from green, the other from yellow oranges. Unfortunately, the samples were so small

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[1]) *Annali Chim. appl.* **1** (1914), 408; *Journ. Soc. chem. Industry* **33** (1914), 710. — *Chem. Ztg. Repert.* **38** (1914), 541. — [2]) See *Chemist and Druggist* **85** (1914), 75. — [3]) Compare *Report* April **1912**, 76, 77. Unlike with the citral determination the oil is here allowed to be in contact with phenylhydrazin for two hours, experiments with decylic aldehyde solutions having shown that with a contact of one hour only the results obtained are too low. — [4]) Concerning distilled West Indian orange oils see *Report* April **1910**, 68.

that they were just only sufficient for the determination of specific gravity and rotation. These values were within the recognized limits of sweet orange oil: —

Oil from green oranges: $d_{15°}$ 0,8515; $\alpha_{D20°}$ + 98° 2′
„ „ yellow „ : $d_{15°}$ 0,8492; $\alpha_{D20°}$ + 97° 22′.

Eucalyptus Oil. Part 10 of the second volume, and part 1 of the third volume of J. H. Maiden's work: *A critical revision of the genus Eucalyptus* (Sydney 1914) contain descriptions of the following species of *Eucalyptus*: *E. gigantea*, Hook. f. (*E. delegatensis*, R. T. Baker; *E. obliqua*, L'Hérit. var. *alpina*, Maiden); *E. longifolia*, Link et Otto (*E. Woollsii*, F. v. M.); *E. diversicolor*, F. v. M. (*E. colossea*, F. v. M.); *E. Guilfoylei*, Maiden; *E. patens*, Benth.; *E. Todtiana*, F. v. M.; *E. micranthera*, F. v. M.; *E. cinerea*, F. v. M. (*E. pulverulenta*, F. v. M. non Sims.; *E. Stuartiana secunda*, F. v. M.; *E. pulverulenta*, F. v. M. var. *lanceolata*, Howitt; *E. Stuartiana*, F. v. M. var. *cordata*, Baker et Smith); *E. c.* var. *multiflora* and *nova anglica* (nov. var.); *E. pulverulenta*, Sims. (*E. pulvigera*, A. Cunn.; *E. rigida*, Hoffmg.; *E. cordata*, Loddiges non Labill.); *E. cosmophylla*, F. v. M. and *E. gomphocephala*, A. P. DC.

Fennel Oil. The use of this oil against vermin is referred to in a short note on page 74.

Galangal Oil. In the course of an examination of galangal oil, E. Fromm and H. Fluck[1]) obtained a fraction of b. p. 171 to 173° containing cineol. When shaken with aqueous concentrated hydriodic acid, fairly stable, dark green crystals of an iodine combination were formed. From cineol (eucalyptol) the same green body was obtained in like manner. A closer examination revealed the fact that this combination is formed only if the hydriodic acid contains free iodine. If it is freed from iodine by shaking with red phosphorus, cineol is converted to dipentene di-iodide, which had been prepared by Wallach and Brass by subjecting well-cooled cineol to the influence of gaseous hydriodic acid. Inasmuch as the dark green iodine combination of cineol is obtained neither with free hydriodic acid nor with pure iodine solution, it is evident that both substances are necessary for its formation. As a matter of fact cineol forms these green crystals instantaneously with acidulated iodine and iodide of potassium solution. This reaction offers so little difficulty that it is even possible to titrate cineol in this manner. To this end 0,2155 g. of cineol are well shaken with 20 cc. of a solution of one-tenth-normal iodine in potassium iodide and a sufficiency of dilute hydrochloric acid, in which process the cristallized combination separates readily. After filtering and washing with cold water, the unused iodine in the filtrate is titrated back with a one-tenth-normal thiosulfate solution, for which purpose 6,55 cc. were required. Therefore 0,2155 g. of cineol used up 13,45 cc. of one-tenth-normal iodine-iodide of potassium solution, or 1 gram molecule cineol 960 cc. normal iodine solution. It follows that the cineol used was of 96 p.c. strength, and that 1 molecule of cineol binds 1 atom of iodine. It is suggested that by this method the amount of cineol in fractions containing more than 60 p.c. of cineol may be determined with certainty. As we have convinced ourselves by experiments, and as was to be expected, it fails whenever, besides cineol, other combinations, such as *f. i.* terpenes, are present, which

[1]) *Liebigs Annalen* **405** (1914), 175, 181.

add iodine. For instance, 0,2 g. of pinene used up 13,7 cc. of one-tenth-normal iodide solution, that is to say, about as much as Fromm and Fluck indicate for 0,2155 g. cineol. Seeing that in eucalyptus and cajuput oils we have to deal with such mixtures, this method is not adapted for the quantitative determination of cineol in these oils.

Presumably the combination just described is really the double combination $C_{10}H_{18}OI_2 + C_{10}H_{18}OHI$, which might be termed cineol di-iodide-hydriodide. According to Fromm and Fluck it is not impossible, that the cineol-di-iodide described by Wallach and Brass does not exist at all, and that these authors may have had to deal with an impure cineol di-iodide-hydriodide.

There were also obtained from galangal oil: 1 to 2 p.c. of a body of the b. p. 208 to 210°. This new substance has the empirical composition $C_{10}H_{16}O$. Nothing further was ascertained concerning the manner of the linking of the oxygen. A sesquiterpene was also isolated from the oil, which is diolefinic, adding 4 atoms of bromine and boiling at 138 to 140° (12 to 15 mm.). It is not identical with the sesquiterpene found in this oil by Schindelmeiser; no addition product is obtained with hydrogen chloride. A second sesquiterpene found in the oil yields a hydrochloride $C_{15}H_{24}\cdot 2HCl$, of the same melting point as cadinene hydrochloride, but on being mixed with the latter it shows a perceptible lowering of the melting point (by about 10°). From the high-boiling parts white needle-like crystals are separated occasionally after prolonged standing; these may be purified from hot alcohol. Their melting point lies at 167°, and they correspond with the formula of a sesquiterpene hydrate $C_{15}H_{26}O$.

According to Horst, eugenol is supposed to be contained in the oil to the extent of 25 p.c, but the authors have failed to establish its presence.

Galbanum Oil. About the composition of this oil little had been published so far; all that was known was that it contained *d*-α-pinene and cadinene. An examination carried out a short time ago by F. W. Semmler and K. G. Jonas[1]) revealed a few further constituents. The oil analysed had the following properties: b. p. 55 to 195° (15 mm.); $d_{25°}$ 0,9353; $\alpha_{D25°} + 8°$; $n_{D25°}$ 1,49395. In the low-boiling parts α-pinene (nitrosochloride, m. p. 107 to 108°) was present, as well as β-pinene (nopinic acid, m. p. 128°). On testing for camphene, a mixture of the optically active terpineols, m. p. 35 and 32°, was obtained, instead of *iso*borneol. The formation of these bodies is explained by an addition of water to pinene, *i.e.* β-pinene. Myrcene was easily established by conversion to camphorene and by production of the α-camphorene tetrahydrochloride[2]). A fraction of the b. p. 100 to 120° (15 mm.) ($d_{22°}$ 0,9504; $\alpha_{D22°} + 10°$; $n_{D22°}$ 1,49181) possessed in a particularly strong degree the peculiar bitter-aromatic odour of galbanum oil and contained a body $C_{10}H_{16}O$; b. p. 105 to 115° (15 mm.); $d_{20°}$ 0,951; $\alpha_D + 6°$; n_D 1,4918. Possibly we have here to deal with a ketone, which is very easily enolizable. On oxidation the fraction yielded a ketonic acid $C_{10}H_{16}O_3$, which, when treated with alkaline solution of bromine, was converted into a dicarboxylic acid $C_9H_{14}O_4$. A fraction obtained by repeated distillation over sodium had the following figures: b. p. 132 to 138° (10 mm.); $d_{19°}$ 0,9282; $\alpha_{D19°} + 33°$; $n_{D19°}$ 1,50526. On the addition of hydrochloric acid gas it furnished *l*-cadinene dihydrochloride. According to Semmler and Jonas it is, however, an open question as to whether in this dextro-rotatory fraction *l*-cadinene is actually present, the laevo-rotation of which is covered by a strongly dextro-rotatory body, or whether the dextro-rotatory sesquiterpene contained

[1]) *Berl. Berichte* **47** (1914), 2068. — [2]) Comp. *Report* October **1913**, 35.

therein is converted into *l*-cadinene only through the influence of hydrochloric acid. The fraction of the b. p. 155 to 165° (15 mm.) ($d_{20°}$ 0,9720; α_D + 22°; n_D 1,50702) contained a new tertiary sesquiterpene alcohol $C_{15}H_{26}O$, which the authors call cadinol. It splits off water readily, forming cadinene. Its dihydrochloride was identical with that of cadinene. Cadinol itself readily forms a dihydrochloride, m. p. 117 to 118°. By means of platinum and hydrogen, cadinene regenerated from the hydrochloride as well as the one produced by splitting off water could be reduced to tetrahydrocadinene, the properties of which are as follows. Tetrahydrocadinene from regenerated cadinene: b. p. 125 to 128° (10 mm.); $d_{20,5°}$ 0,8838; $\alpha_{D20,5°}$ — 20°; $n_{D20,5°}$ 1,48045. Tetrahydrocadinene from artificial cadinene: b. p. 125 to 128° (10 mm.); $d_{18,5°}$ 0,8846; $\alpha_{D18,5°}$ — 15°; $n_{D18,5°}$ 1,48221. Tetrahydrocadinene from dihydrochloride melting at 118°: b. p. 125 to 128° (10 mm.); $d_{21,5°}$ — 52°; $n_{D21,5°}$ 1,48094.

The colour reaction indicated by Wallach[1]) could be observed neither in the cadinene regenerated from its dihydrochloride, nor in the one obtained from cadinol by splitting off water. On the other hand, a cadinene fraction distilled from copaiba oil showed the blue coloration. Semmler and Jonas suspect that the blue colour is due to, or caused by, an admixture, and cannot be considered a characteristic of cadinene.

Geranium Oil. D. R. Mason[2]) describes the cultivation of the geranium plant and the production of geranium oil in Algeria. There is nothing essentially new in the paper, requiring anything but the mention of the treatise in question.

In Mason's opinion it might, perhaps, be possible to start geranium plantations succesfully in southern California.

Gurjun balsam Oil. From the examinations of Deussen and Philipp[3]) it was known that gurjun balsam oil contains the two sesquiterpenes, α- and β-gurjunene and that, by oxidation with permanganate of potassium in acetone solution gurjunene ketone results, characterized by its semicarbazone. This reaction was successfully made use of in our laboratories in the determination of added gurjun balsam oil in otto of roses[4]). Further particulars concerning the properties and derivatives of the sesquiterpenes of gurjun balsam oil may be found in a very elaborate paper by F. W. Semmler, K. E. Spornitz and W. Jakubowicz[5]), who found that crude gurjunene consists, to the extent of about 67 p.c., of strongly laevo-rotatory tricyclenegurjunene (α-gurjunene) and of about 33 p.c. strongly dextro-rotatory tricyclic gurjunene, of the cedrene type. In order to produce this tri*cyclo*gurjunene (β-gurjunene) in a pure form, crude gurjunene was treated with chromic acid in glacial acetic acid solution, in which process the original laevo-rotation (α_D — 55°) was converted into dextro-rotation. Presumably the chromic acid decomposes the laevo-rotatory hydrocarbon first, after which the dextro-rotatory parts are attacked. By repeating the oxidation, in the last place with permanganate of potassium in acetone solution, a fraction was obtained which showed the following properties after distillation over sodium: b. p. 120 to 123° (13 mm.). d 0,9348; α_D + 74,5°; n_D 1,50275. This is the pure, dextro-rotatory tricyclic gurjunene of the cedrene type, which the authors call tri*cyclo*gurjunene; in the course of oxidation of this sesquiterpene, with chromic acid as well as with permanganate of potassium, a considerable percentage of the gurjunene ketone, described by Deussen and Philipp, was

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[1]) Blue coloration when shaking a solution of cadinene in chloroform or glacial acetic acid with one drop of concentrated sulphuric acid. *Liebigs Annalen* **238** (1887), 87. — [2]) *Americ. Perfumer* **9** (1914), 192. — [3]) *Liebig's Annalen* **369** (1909), 56; **374** (1910), 105; *Report* April **1910**, 146; October **1910**, 71. — [4]) *Report* April **1912**, 109. — [5]) *Berl. Berichte* **47** (1914), 1029, 1141.

obtained. The authors succeeded in producing, in solid form, the ketone which had been regenerated from the semicarbazone m. p. 237° with phthalic acid anhydride. M. p. 43°; b. p. 163 to 166° (10 mm.); $d_{20°}$ 1,017; α_D + 123°; n_D 1,52700. Semmler and his collaborators assume that the gurjunene ketone possesses the empirical formula $C_{15}H_{22}O$, and not $C_{15}H_{24}O$, as indicated by Deussen and Philipp, although the molecular refraction, which shows a very big increment, really answers the formula $C_{15}H_{24}O$ better: calculated for $C_{15}H_{22}O/\overline{1}$ 64,63, found 65,90. Increment 1,27. By reduction with sodium and alcohol the ketone yields gurjunene alcohol, $C_{15}H_{24}O$: m. p. 104°; b. p. 155 to 159° (11 mm.); d 1,001; α_D + 34°; n_D 1,51859.

The ketone could not be reduced further. In the reduction of tri*cyclo*gurjunene with platinum and hydrogen only 2 atoms of hydrogen were added, tri*cyclo*dihydrogurjunene being formed: b. p. 120° (8 mm.); d 0,9258; α_D — 37,5°; n_D 1,49775. Tri*cyclo*gurjunene may also be obtained from gurjunene ketone semicarbazone, by heating the semicarbazone to 160° in a sealed tube with sodium alcoholate and alcohol. The hydrocarbon resulting from this method showed the same properties as the tri*cyclo*gurjunene, with the exception of the rotation which was found to be reduced. That, nevertheless, tri*cyclo*gurjunene, even though inverted, had been obtained was proved by the fact that in oxidizing with permanganate of potassium gurjunene ketone resulted once more. On heating gurjunene in the sealed tube to 290° only a slight inversion was noticeable. As is the case with all sesquiterpenes resembling cedrene, the tri*cyclo*gurjunene does not yield Turner's colour reaction. By fractionated distillation of the crude gurjunene, a sesquiterpene of the following properties was obtained: b. p. 114 to 116° (10 mm.); $d_{20°}$ 0,918; α_D — 95°; n_D 1,5010. This fraction consists of fairly pure tricyclenegurjunene (α-gurjunene). In the reduction it only adds two atoms of hydrogen; when oxidized it does not yield gurjunene ketone, but responds in a very pronounced manner to Turner's colour reaction. By heating in a sealed tube complete inversion was attained. Neutral and acid bodies were obtained as oxidation products of tricyclenegurjunene, but nothing further is known about these bodies.

In the reduction with platinum and hydrogen, crude gurjunene only adds 2 atoms of hydrogen, from which the authors conclude that it cannot contain any bicyclic sesquiterpenes.

Hop Oil. In a very complete paper published by F. Rabak[1]) on hops and the relation between the composition of hop oil, and the hops used in its distillation, we find a few notes on the composition of hop oil. As constituents of this oil dipentene, myrcene, linalool, *iso*nonylic acid (?), and humulene (a mixture of i-α- and β-caryophyllene) had been known so far, to which list Rabak now adds the following bodies: free formic acid (characterized by reduction of mercuric chloride to mercurochloride), heptylic acid (œnanthylic acid) (silver salt) and valeric acid (silver salt), esterified formic acid, acetic, decylic (caprinic), nonylic (pelargonic), octylic (caprylic), œnanthylic and butyric acids. In order to prove their presence, Rabak added little by little to the solution of the acid mixture, which had been neutralized with potassium hydroxide, a solution of nitrate of silver, carefully ascertaining the silver percentage of the precipitate after every addition. Formaldehyde was contained in the saponified oil (red coloration with Lebbin's solution [a 5 p.c. solution of resorcinol in a 40 to 50 p. c. solution of sodium hydroxide]). Besides myrcene and humulene, myrcenol also occurs in hop oil. Presumably it is present in the free

[1]) *Journ. of agricult. Research*, Departm. of Agric., Washington, 2 (1914) 115.

state as well as in the form of œnanthylic, caprylic and pelargonic esters. The constants of the myrcenol of hop oil agree well with those of the synthetic product. The quantitative composition of hop oil may be approximately as follows: 30 to 50 p.c. of myrcene; 15 to 20 p.c. humulene, and 20 to 40 p.c. of myrcenol esters.

Illustrating his paper with numerous tables and graphic plates, Rabak arrives at the following summary on the

Properties of hop oils of different origin:

Origin	Year	Yield p.c.	$d_{20°}$	$n_{D20°}$	acid v.	ester v.	solubility in 94 p.c. alcohol
California[1]) . .	1907	0,24	0,823	1,4856	2,3	44,4	5,4 Vol.
	1908	0,35	0,836	1,4738	1,7	45,5	4 „
	1909	0,38	0,839	1,4730	1,8	46,8	3,6 „
Oregon	1907	0,20	0,8343	1,4802	1,6	57,0	4,6 „
	1908	0,32	0,838	1,4730	1,0	50,2	3,3 „
	1909	0,30	0,8433	1,4705	2,8	56,0	3 „
NewYork . . .	1907	0,16	0,862	1,4804	3,6	61,0	3,5 „
	1908	0,14	0,837	1,4756	2,1	47,0	3,5 „
	1909	0,15	0,8777	1,4800	2,5	51,8	3,7 „
Washington . .	1908	0,36	0,850	1,4763	1,0	51,8	3,5 „
	1909	0,38	0,8464	1,4734	1,5	53,8	3,3 „
Saaz(Bohemia)	1907	0,32	0,855	1,4905	1,5	52,8	4 „
	1908	0,23	0,824	1,4852	1,0	52,8	6 „
	1909	0,24	0,861	1,4829	3,0	55,3	4 „

The oils of different origin contain the same component parts in varying proportions. The most valuable part is the ester to which, according to Rabak, the oil owes its aroma in a very large measure. American hop varieties do not seem to excel as regards fine odour.

Oil of Lantana Camara. D. D. Kanga[2]) reports on the oil from *Lantana Camara*, L.[3]), a shrub-like verbenacea originating from tropical America, and growing wild in enormous quantities in British India. This plant has become a veritable pest in the southern parts of India. In the districts round Bombay it is called "Ghaneri", the people also calling it "Heliotrope of the lower land". The properties of the oil obtained from dried and fresh flowers are as follows: —

Oil from:	*dried* and from *fresh flowers*		from *leaves*
colour	yellow	yellow	yellow
odour	savin-like	same	same
yield	0,07 p.c.	—	0,2 p.c.
density	$d^{26°}_{15°}$ 0,915	—	$d^{24°}_{24°}$ 0,9211
α_D	+ 23,9°	—	+ 1,96°
$n_{D26°}$	1,4987	1,5031	$n_{D27°}$ 1,48933
sap. v.	10	—	—
sap. v. after acetylation	43,6	—	—

[1]) Average figure for 5 oils from five different Californian localities. — [2]) *Arch. der Pharm.* 252 (1914), 1. — [3]) Comp. *Report* October 1909, 73; October 1913, 67.

Oil of Lavandula dentata. In our *Reports* October **1905** (p. 40) and April **1908** (p. 62) we published short notes on an oil which had been distilled by us, presumably from the flowers of *Lavandula Stœchas*, L. These flowers had been sent us at the time under this designation from Spain. Doubts having arisen meantime as to the correctness of these indications, we requested Dr. Giessler, custodian of the Botanical Institute of Leipzig University, to make a close botanical examination of the material in question. The result was that the mother-plant was found to be, not *Lavandula Stœchas*, but *Lavandula dentata*, L. It was recognized by its long-stalked inflorescences and its pinnate leaves, with rounded dentation. *Lavandula Stœchas* has short-stalked inflorescences and leaves with curled margin.

We may as well repeat the informations given at the time concerning the composition of the oil. It was of a brownish yellow colour and had a camphory odour. $d_{15°}$ 0,9620; α_D + 35° 30′; $n_{D20°}$ 1,47909; acid v. 5,16; ester v. 13,1; ester v. after acetylation 67,9; soluble in 2 volumes and more of 70 p.c. alcohol; the diluted solution became opalescent owing to separation of paraffin. As component parts of the oil *d*-camphor (m. p. 175 to 175,5°; oxime, m. p. 117 to 118°; semicarbazone, m. p. 231°) and *d*-fenchone (oxime, m. p. 165°) were found. Possibly fenchylalcohol occurs in the oil too.

Lavender Oil. As has been mentioned repeatedly in technical literature[1]), lavender oils produced in the modern manner, by means of dry steam distillation, are much less readily soluble than those obtained by the old method, *i. e.* by distillation with water. J. G. R. Francois[2]) attributes this phenomenon to the presence of wax-like substances which are carried over in consequence of the quicker and more energetic distillation, whereas with the ordinary method of production in vogue in the South of France this does not seem to be the case. It is said that, when stored, the oils become more soluble after some time, owing, presumably, to the wax-like substances settling little by little. This is confirmed from another quarter[3]). An oil which originally required 6,5 to 7 volumes of 70 p.c. alcohol for a clear solution, dissolved in 4 volumes after 8 months; another oil at first in 5 volumes, and after about three months in 3,5 volumes only. We have not come across such oils so far. The lavender oils under our own observation became either less readily soluble with age, or else there was no noticeable alteration at all. The presence of "wax-like" bodies in oils distilled with dry steam seems to us highly improbable and we have never noticed anything like it in such distillates.

On page 68 of our *Report* October **1913** we mentioned a lavender oil which had been distilled in Comisa[4]) (island of Lissa) and which was remarkable owing to its extraordinarily high ester percentage (57,1 p.c.). A still higher ester percentage, namely 61,6 p. c., has been observed since then in an oil distilled from dried flowers in Comisa[5]). It had the following properties: d 0,899, α_D — 8° 30′, soluble in 4 volumes of 70 p.c. alcohol.

Lemongrass Oil. We have often reproduced in these *Reports*[6]) publications of the Imperial Institute in London about badly soluble East Indian lemongrass oils.

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[1]) Comp. *i. a. Report* April **1907**, 66. — [2]) *Perfum. Record* **5** (1914), 147. — [3]) *Ibidem* 264. — [4]) The town of Comisa is meant, on the island of Lissa. An island of Comisa, as had been mentioned in the report in question, does not exist. — [5]) *Perfum. Record* **5** (1914), 130. — [6]) Comp. *Report* April **1912**, 89; April **1913**, 71.

Meantime the above-named Institute[1]) has examined five more distillates originating from various parts of the Madras Presidency. Only two of these oils were soluble in 70 p.c. alcohol, *viz.*, one from Kayankulam (2 vols., 68,5 p.c. of aldehyde) and one from Alwaye (1,75 vol., 77 p.c. of aldehyde), whereas the remaining three (2 from Alwaye and 1 from Cochin) did not give a clear solution at all in 70 p.c. alcohol. Of 80 p.c. alcohol $^2/_3$ vol. was required for a clear solution, but turbidity set in whenever more of the solvent was added. As indifferent solubility had never been observed in East Indian lemongrass oils formerly, it was surmised that the method of distillation had been altered[2]) or that in such cases a different variety of grass was used as raw material. In order to probe the matter, the Imperial Institute caused two samples of oil to be sent, one from white-stalked grass, the other distilled from the red-stalked variety. Both kinds grow wild in the Madras district, but the red-stalked grass is also cultivated to a fairly large extent in northern and central Travancore; wild as well as cultivated grass, however, appears to be used indiscriminately for distillation purposes.

The oil from the white-stalked grass was of yellow colour, and in odour as well as in its other properties it resembled citronella oil more than lemongrass oil: $d_{15°}$ 0,909; α_D — 10° 50′; aldehyde percentage (bisulphite method) 9 p.c.; soluble in 0,8 volumes and more of 80 p.c. alcohol, in 4 volumes slight turbidity; not soluble in 70 p.c. alcohol. A botanical examination will afford further particulars as to the mother-plant.

The oil obtained from red-stalked grass was reddish brown in colour and had the typical lemongrass oil odour: $d_{15°}$ 0,925; aldehyde contents (bisulphite method) 71,5 p.c. It did not give a clear solution with 5 volumes of 70 p.c. alcohol, but dissolved readily in 0,8 volume and more of 80 p.c. alcohol; but on addition of 5 volumes of the solvent turbidity supervened. When rectified with steam 78,7 p.c. of the oil passed over. The distillate contained 81 p.c. of aldehyde and dissolved clearly in 2,4 volumes, and more, of 70 p.c. alcohol. The residue consisted of an oil of reddish brown colour, and of great viscosity. From the above figures the Imperial Institute draws the conclusion that the indifferent solubility of the original oil is probably caused by its having been distilled too long, causing bodies to pass into the oil which were less volatile, and but sparingly soluble. Nothing is said as to whether this variety is also to be subjected to a closer botanical examination.

A so-called West Indian lemongrass oil, distilled in Annam, had the following properties[3]): $d_{15°}$ 0,8846; α_D — 0° 4′; soluble in 0,25 volumes of 80 p.c. alcohol, on further addition of the solvent milky turbidity set in; the oil contained 75 p.c. of citral. According to Murat there are extensive plantations of *Andropogon citratus* in Annam.

For a lemongrass oil from Mayotte, Roure-Bertrand Fils[4]) give the following constants: $d_{15°}$ 0,8917; α_D — 0° 22′; soluble in 0,4 volumes of 80 p.c. alcohol. When adding more than 2 volumes, strong turbidity set in. The solution of the oil in 90 p.c. alcohol began to opalize after 2,5 vols. It is here a case of a so-called West Indian lemongrass oil which contained 87 p.c. of constituents reacting with sodium bisulphite.

Lemongrass oils of this origin have been mentioned by us before now[5]).

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[1]) *Bull. Imp. Inst.* **12** (1914), 222. — [2]) Comp. *Report* October **1913**, 69. — [3]) *Berichte von Roure-Bertrand Fils* April **1914**, 10. — [4]) *Ibidem* 12. — [5]) *Report* April **1913**, 72; October **1913**, 69.

Lime Oil. The Imperial Institute of London[1]) reports on a lime oil produced by distillation in the Fiji islands. The oil was of light yellow colour and possessed the characteristic odour of the product as distilled in the West Indies. Specific gravity and rotation also were in accordance with West Indian oil: $d_{15°}$ 0,868; $\alpha_{D21°}$ + 37° 6'.

Oil from Lophanthus rugosus. On page 73 of our *Report* October **1913** we described the oil from *Lophanthus anisatus* (N. O. *Labiatæ*). P. de Vilmorin and F. Levallois[2]) now report on the oil of another *Lophanthus* species, namely *L. rugosus*, Fisch. et Mey. The genus *Lophanthus* comprises 6 to 8 species which occur in northern America and eastern Asia. Whereas *L. anisatus* originates from northern America, *L. rugosus* is a plant which grows wild, and is also cultivated, in eastern Asia, and which may attain a height of 1,20 m. (40 to 50 inches). The yield of oil amounts to about 0,23 p.c. (calculated for fresh herb?). The inflorescences contain a little more oil, up to 0,5 p.c. The oil is an amber-coloured liquid, soluble in every proportion of 95 p.c. alcohol, in 1,2 vol. of 90 p.c., in 4,5 vols. of 85 p.c. and in 23 vols. of 70 p.c. alcohol. $d^{40°}_{15°}$ 0,962 to 0,967; $[\alpha]_D$ + 4,89 to + 6,19°; sap. v. 3,7; sap. v. after acetylation 7,4. The oil reacts slightly with bisulphite. About 8 p.c. boil from 60 to 63° (10 mm.), 2 p.c. from 63 to 90° (10 mm.), 86 p.c. from 90 to 94° (10 mm.) and about 4 p.c. above 100°, with partial decomposition. Methylchavicol appears to be the chief constituent, it was characterized by being converted into anethole, m. p. abt. 20°. The fractions of the b. p. about 60° (10 mm.) contain presumably *d*-limonene: b. p. 174°; $d^{15°}_{4°}$ 0,8494; $[\alpha]_D$ + 106,8°; tetrabromide, m. p. 104°; nitrosochloride, m. p. 103 and 105° respectively. When the nitrosochloride was purified, a body of the m. p. 154° was obtained, the corresponding hydrocarbon of which the authors have not yet ascertained.

Mastic Oil. For some considerable time *d*-pinene[3]) had been suspected in mastic oil. In order to settle the question the fractions that passed over first in the process of distillation were collected by us separately and examined very closely. They had the following properties: b. p. 156 to 170°; $d_{15°}$ 0,8599; α_D + 38° 57'; $n_{D20°}$ 1,46925.

The peculiar balsamic odour pointed to the presence of pinene and phellandrene. The oil, however, did not yield any phellandrene reaction when treated with nitrous acid. A fraction of the b. p. of 156 to 157° ($d_{15°}$ 0,8615; α_D + 39° 14') gave an infinitesimal precipitate of a nitrosochloride, m. p. 106° (benzylamine base, m. p. 123 to 124°). The slight yield of nitrosochloride from such a strongly active pinene fraction made the simultaneous presence of active and inactive α-pinene probable. In order to establish proof of both bodies an attempt was made to obtain the corresponding pinonic acids by means of permanganate oxidation. In what passed over first of the resulting acid mixture, traces of an acid, melting indifferently between 95 and 98°, could be proved, which was perhaps identical with pinonic acid obtainable from inactive pinene, and melting at 104°. Besides this, an acid of the m. p. 183 to 185° was also isolated. From the main fraction of the acid mixture, inspite of inoculation with inactive pinonic acid, m. p. 104°, crystals of the active acid only, melting at about 70°, could be obtained: $[\alpha]_D$ + 90,15° (8,8717 p.c. solution in chloroform); semicarbazone, m. p. 204°. Even a close examination of the mother-liquors yielded no acids melting at 104°. From the semicarbazone, produced therefrom with a melting point of 195 to 200°, a semicarbazone melting at 190 to 191° was isolated, which proves that the crude

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[1]) *Bull. Imp. Inst.* **12** (1914), 227. — [2]) *Bull. Soc. chim.* IV. **15** (1914), 342. — [3]) Gildemeister and Hoffmann, *The Volatile Oils*, 1st Ed., p. 496.

derivative, and therefore the mother-liquors as well, were not homogenous bodies. It would appear, therefore, that in the oxidized hydrocarbon fraction yet another hydrocarbon is present, apart from considerable quantities of *d*-α-pinene and traces of inactive pinene. Fractions of the b. p. 159 to 162°, in which β-pinene or sabinene might have been suspected, yielded only oxalic acid upon oxidation with permanganate, instead of the oxidation-products characteristic for these bodies.

In the lowest boiling fractions, therefore, *d*-α-pinene occurs chiefly, besides traces of inactive α-pinene; moreover, there appears to be present yet another terpene, which could not be characterized so far.

Musk seed Oil, see Ambrette seed Oil, p. 7.

Neroli Oil. According to informations of an American contemporary[1]), the production of neroli oil and orange flower water in Tunis is confined to the district of Nabeul, where from 200000 lbs. of orange flowers about 200 lbs. neroli oil and 74000 to 85000 quarts of orange flower water are distilled annually. These products are disposed of in Tunis as well as abroad, more especially in France. Statistically nothing is known about the exports, as the Customs authorities include neroli oil in one figure along with other oils.

Oil of Ocimum pilosum. Kshitibhusan Bhaduri[2]) reports on the oil of *Ocimum pilosum*, Roxb.[3]) (N. O. *Labiatae*). It is contained in fresh seeds as well as in the leaves, but not in dried seeds. In the author's opinion this is due to the very volatile oil evaporating or resinifying when the seeds are dried. It is a pale yellow, very mobile liquid which smells almost exactly like lemongrass oil; on evaporation it leaves a resinous residue. The properties are: $d_{25.5°}$ 0,8872; α_D —3,7°; $n_{D21.5°}$ 1,4843. It contains 34 p.c. of citral and 41 p.c. of citronellal (characterized by the condensation products with pyruvic acid and β-naphthylamine), cineol (green, glossy crystals upon addition of a solution of iodine in iodide of potassium), limonene (characterized by its constants and the colour reaction with ferric chloride and hydrochloric acid), thymol and furthermore some high-boiling fractions, b. p 205 to 230°. On being shaken with an aqueous solution of sodium sulphite and sodium carbonate, 75 p.c. of the oil were absorbed.

Orris Oil. Some little while ago a sample of liquid orris oil was submitted to us for analysis; its properties were found to differ materially from those of a normal oil. Its constants were: $d_{15°}$ 0,9644; α_D + 12° 14'; $n_{D20°}$ 1,49383; acid v. 0,6; ester v. 96,1. Insoluble in 10 volumes of 80 p.c. alcohol; soluble in 0,2 vol. and more of 90 p.c. alcohol.

For liquid orris oil, Gildemeister[4]) gives the following values: $d_{15°}$ 0,93 to 0,94; α_D + 14 to + 30°; $n_{D20°}$ about 1,495; acid v. 1 to 8; ester v. 20 to 40; soluble in 1 to 1,5 vol. and more of 80 p.c. alcohol.

As will be seen, specific gravity as well as ester value of the sample were higher, rotation and acid value lower, and solubility worse, than required of a pure orris oil. Closer examination showed the sample to have been adulterated with about 50 p.c. of castor oil.

When distilled with steam, about 40 p.c. passed over, showing the following figures: $d_{15°}$ 0,9600; α_D + 20° 20'; acid v. 0,3; ester v. 5,6. Insoluble in 10 volumes of

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[1]) *Oil, Paint and Drug Reporter* **86** (1914), No. 4, p. 36. — [2]) *Journ. Americ. Chem. Soc.* **36** (1914), 1772. — [3]) According to the Index Kewensis *Ocimum pilosum*, Willd. is synonymous with *O. Basilicum*, L. *O. pilosum*, Roxb. does not occur in the Index. — [4]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 270.

80 p.c. alcohol, therefore the distillate did not agree either with the figures indicated by Gildemeister for pure oil. Presumably there was a further adulteration, which was not characterized more particularly. The distillation residue (about 53 p.c.) showed the characteristic behaviour of castor oil: $d_{15°}$ 0,962; α_D + 4° 30′; acid v. 0,3; ester v. 174,1. insoluble in light petroleum.

Palmarosa Oil. Although Java is not known as a country producing palmarosa oil, a few samples received by us from that island prove that the production of a good marketable article is well understood. The properties of the oils in question were within the recognized limits: $d_{15°}$ 0,8906 to 0,8920; α_D + 0° 30′ to + 0° 42′; acid v. 1,2 to 1,8; ester v. 37,5 to 51,6; ester v. after acetylation 272,7 to 276,8, corresponding with 94,3 to 96,0 p.c. of total geraniol; soluble in 3 to 3,5 volumes and more of 60 p. c. alcohol. In some instances the diluted solution showed slight opalescence. The geraniol percentage reached a height observed only in exceptional cases even by the best Indian oils.

Oil of Grains of Paradise. Very little is known about the oil from grains of paradise, the seeds of *Amomum Melegueta,* Roscoe, belonging to the *Zingiberaceae*[1]). It may, therefore, be of interest if we give the values of an oil distilled by ourselves. The yield was 0,5 p.c. The oil was of light brown colour and of a peculiar odour which it would be difficult to describe. $d_{15°}$ 0,8970; α_D — 3° 10′; $n_{D20°}$ 1,49116; acid. v. 2,7; ester v. 41,2; ester v. after acetylation 63,9. It does not dissolve in 90 p.c. alcohol, but is clearly miscible, at first, in 95 p. c. alcohol, but from 1 volume of alcohol, turbidity sets in which decreases upon further addition of the solvent but, does not completely disappear. About 16 p.c. of the oil reacted with a 3 p.c. solution of caustic soda. We have not been able to ascertain anything definite about the nature of the absorbed parts of the oil, as we had not enough material at our disposal; to judge from the odour, we had to deal with phenols, amongst which eugenol was also represented.

Peppermint Oils. W. Himmelbaur[2]) reports on deterioration and subsequent disease of *Mentha* plantations. It was a question of slips of *Mentha piperita* (L. ex parte) Huds. var. *officinale,* Sole, which were grown in a long and narrow border in an experimental nursery in Prague. The location was unfavourable inasmuch as on one side it was only 1,5 m. distant from a high wall, and was shaded on the other side by a high tree. Moreover, the whole plantation was quite close to inhabited buildings. Another cultivation experiment was carried out in Korneuburg, where *Mentha arvensis* f. *piperascens,* Mal. (= *canadensis* f. *piperascens,* Briq.) had been planted. The plot of ground was quite unshaded, but in close proximity to some gas works. Moreover, the situation in general was rather dry and exposed to the winds. In the beginning of August a weakening of the growth made itself felt in consequence of these unfavourable conditions. In Prague, damage through smoke first, and later an attack of *Puccinia Menthae,* the well known fungus disease, were noticeable; in Korneuburg, however, the attack of *Puccinia Menthae* set in first, and damage by smoke later on. Himmelbaur describes the progress of the disease with many illustrations. As compared with healthy plants it was noticed that the leaves showed little drops of a yellow substance, and many crystals. The former consisted of fatty oil, the crystals presumably of the

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[1]) Comp. Gildemeister and Hoffmann, *The Volatile Oils,* 2nd ed., vol. II. — [2]) *Zeitschr. f. d. landwirtsch. Versuchswesen in Österreich,* **1914**, No. 3/4.

glucoside hesperidin contained chiefly in the *Rutaceae*. Under normal conditions these two bodies do not occur in *Mentha* in such abundant quantities.

The chief damage to be noticed was the reduction in the activity of the chlorophyll apparatus. As a further noticeable symptom of the deep-seated disturbance, the superabundance of bodies such as hesperidin is to be mentioned. Hesperidin must be looked upon as a vegetable dross in the process of metabolism, as it is never taken up again. Simultaneously all protective bodies against fungi are affected, so that an attack of fungi may easily take place or that the resisting power against damage by smoke is reduced. Quickly passing smoke does not hurt healthy plants.

As the author correctly observes, the peppermint plant is rather particular as regards location and condition of soil. It requires a moderately moist and at the same time light and sunny situation, protected from wind.

Cultivation experiments with various kinds of *Mentha* in Austria are described on page 64.

A. Wöhlk[1]) reports on comparative examinations of some peppermint oils of commerce along with control tests of the ordinary menthol determination. As the results of his experiments, as admitted by himself, do not contribute anything new to the chemistry of peppermint oil, we need only mention that, according to Wöhlk, peppermint oil may be rectified *in vacuo* without material loss, but that this process offers no advantage over ordinary distillation by steam.

The indifferent results obtained occasionally in the determination of ester as well as of total menthol in peppermint oil are perhaps due, according to H. W. Redfield[2]), to insufficient cooling when boiling the oil with acetic acid anhydride or with alcoholic potash lye, whereby possibly some of the ester may escape through the condenser and so become lost for determination purposes. In order to arrive at a definite conclusion, Redfield made some comparative tests, using different reflux condensers for the experiment in question. He used an Allihn, a Chamot-Soxhlet and a Fritz Friedrichs condenser. The results with the two last-named condensers were identical, whereas the Allihn apparatus was evidently insufficiently cooled, for the percentage of total menthol was 4,87 p.c. below the values ascertained by means of the other instruments; with ester menthol the difference only amounted to 0,33 p.c.

Compare also the paragraph on page 68 of this *Report*.

Peppermint Oil, Japanese. The Japanese Parliament[3]) has had to deal with a Bill which, if not actually a monopoly, amounted as a matter of fact to little less than the placing of peppermint business under effective State control. The proposed Bill in its main features runs as follows: —

Persons occupied in the cultivation, manufacture and sale of peppermint are to form co-operative production societies, in accordance with the terms of the Act on co-operative production societies.

All persons who have not joined any of these co-operative production societies shall be prohibited from taking part in the cultivation, manufacture, or sale of peppermint.

If the peppermint co-operative production societies contemplate the export of peppermint, they shall be obliged to join in unions for their respective districts, and to establish a central union in Tokyo.

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[1]) *Berichte d. deutsch. pharm. Ges.* **24** (1914), 292. — [2]) *Journ. Ind. Eng. Chemistry* **6** (1914), 401. — [3]) *Nachr. f. Hand., Ind. u. Landw.* **1914**, No. 51, p. 5.

Evidently the object aimed at with this Act is to create a central body comprising all domestic peppermint producers and dealers, so as to enable them to make a firm stand against the peppermint exporters. In this manner it is hoped to prevent the latter, comprising only about 3 to 4 firms, from forming a ring with a view to regulating purchase prices, a combine against which the farmers would be powerless.

The Bill was brought in but a few days before the close of the session. Whether it will make its appearance once again next session remains to be seen. As the adoption of such an Act would undoubtedly make its influence felt on the course of prices of peppermint, parties interested in this article will follow the fate of the Bill with particular attention.

According to K. Irk[1]) the Japanese peppermint plant grows very well in Hungary. He succeeded in propagating slips of *Mentha canadensis* var. *piperascens,* obtained from Berlin-Dahlem in 1911[2]). The oil distilled in 1913 from herb produced by slips had the following properties: d_{15}^{25} 0,8968; n_{D25} 1,4606; ester v. 19,6; ester menthol 5,54 p. c.; free menthol 75,58 p. c.; total menthol 81,12 p. c. The herb grown from seeds yielded an oil showing α_D — 34,14° and containing 76,01 p.c. of total menthol. As will be seen, plants grown from seed contain less menthol than those reared from slips.

Peru Balsam Oil. About the composition of this oil, see page 58 of this *Report.*

Oil of Phoberos cochinchinensis. According to Roure-Bertrand Fils[3]), *Phoberos cochinchinensis,* Lour. *(Scolopia cochinchinensis,* Clos., N. O. *Flacourtiaceae)* is a tree of a little more than 3 m. high, occurring in Annam, and provided with thorns. Customs authorities call this tree *Citrus montana.* 100 kilos of green leaves and stalks are said to yield upon distillation about 90 g. (= 0,09 p.c.) of volatile oil, of the following properties: $d_{15°}$ 0,9042; α_D + 3° 2′; acid v. 2,5; ester v. 51,1; ester v. after acetylation 127,9; soluble in 1/3 volume of 85 p.c. alcohol, the solution showing turbidity later on; soluble in every proportion of 90 p. c. alcohol. In its odour the oil resembles Portugal oil (sweet orange oil).

Pine-needle Oils. In a series of essays, A. W. Schorger[4]) describes the needle oils of various American conifers. So far hemlock or spruce pine-needle oils and cedar leaf oil were chiefly produced. The value of the yearly consumption hereof is estimated by Schorger to reach $ 50000.—. The yearly consumption of spruce pine-needle oil amounts to about 40 to 50000 lbs., and of cedar leaf oil to about 15 to 20000 lbs. Spruce oil is mostly used for perfuming boot polishes and cart grease.

Schorger points out the possibility of distilling other pine-needle oils in considerable quantities, though he questions whether these oils would be of use in commerce. In the United States, when cutting down pine forests, the tops of the trees are left lying about or are burnt. In this manner much material is lost. For this reason Schorger has examined the oils of a number of American pine trees, in order to ascertain whether it would be advisable to distil the waste material in question.

With a view to ascertaining the connection between the anatomical structure of the leaves and the yield in oil, he examined transverse sections of the needles of *Pinus palustris, P. heterophylla* and *P. ponderosa,* finding that the needles of the first-

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[1]) *Pharm. Zentralh.* **55** (1914), 459. See also p. 65 of this *Report.* — [2]) Comp. *Report* April **1911**, 92. — [3]) *Berichte von Roure-Bertrand Fils* April **1914**, 7. — [4]) *Journ. Ind. Eng. Chemistry* **6** (1914), 723, 809, 893; **7** (1915), 24.

named species, which yield the largest percentage of oil (0,401 p.c.), contain five large oil ducts. The needles of *P. heterophylla* (yield 0,271 p.c.) have 10 small ducts, whereas in the needles of *P. ponderosa*, which show the smallest yield (0,112 p.c.), only 2 oil ducts are to be found. The illustrations contained in the original paper clearly demonstrate these differences.

It was found useful to disintegrate the material to be distilled, the yield being increased thereby. Moreover, distillation proceeds more rapidly and more material can be filled into the stills. It would be useless to distil the needles by themselves, as the oil obtained therefrom does not differ in the least from the oil produced by needles and twigs together. The still was an ordinary cylindrical copper boiler with double bottom. A charge, at ordinary temperature, amounted to 350 lbs. Heated, however, *i. e.* when the water was already boiling and the twigs were surrounded by steam, when filled into the still, it was possible to pack 400 lbs. into the apparatus. The first fractions of oil passed over after 2 to 3 hours, the speed of distillation was about $2^1/_2$ gallons an hour. After 7 to 8 hours distillation was completed.

An oil distilled in the Florida National Forest in June 1912 from needles and twigs of *Pinus heterophylla*, Ell. (Cuban pine) showed the following figures: $d_{15°}$ 0,8877 to 0,8894; $\alpha_{D28°}$ — 32,09 to — 35,67°; $n_{D15°}$ 1,4845 to 1,4869; acid v. 0,69; ester v. 10,16; ester v. after acetylation 46,26 to 53,81; yield 0,271 p.c. For the needle oil (yield 0,193 p.c.) the figures were: $d_{15°}$ 0,8895; $\alpha_{D28°}$ — 36,54°; $n_{D15°}$ 1,4880; acid v. 0,78; ester v. 8,75; ester v. after acetylation 43,46. The oil contained furfurol (colour reaction with aniline hydrochloride), 3,9 p. c. of *l*-α-pinene (nitrolpiperidine, m. p. 117 to 118°), 10 p. c. *l*-camphene (conversion to *iso*borneol and camphor), 35,4 p.c. *l*-β-pinene (nopinic acid, m. p. 125°), 8,3 p.c. dipentene (dihydrochloride, m. p. 49°; tetrabromide, m. p. 115 to 117°; the oil may possibly have contained some limonene too), esterified and free *l*-borneol (14 p.c., m. p. 201 to 202°, regenerated from acid phthalate), caprylic (?) and caprinic (?) acids (silver salts), and about 19 p.c. of cadinene. The cadinene hydrochloride melted at 118° and rotated to the left, whereas the cadinene fraction (b. p. 270 to 280°) showed α_D + 14,76°.

From needles and twigs of *Pinus palustris*, Mill. (long leaf pine) Schorger distilled 0,401 p.c. of an oil of the following properties: $d_{15°}$ 0,8829 to 0,8849; $\alpha_{D28°}$ — 26,38 to — 30,49°; $n_{D15°}$ 1,4818 to 1,4824; acid v. 0,66; ester v. 6,75; ester v. after acetylation 36,53 to 46,37. Component parts: furfurol (colour reaction with aniline hydrochloride); 8,6 p.c. *l*-α-pinene (nitrolpiperidine, m. p. 119°); about 14 p.c. of *l*-camphene (conversion to *iso*borneol, m. p. 207 to 210°); 44 p.c. of *l*-β-pinene (nopinic acid, m. p. 126 to 127°); 5 p.c. dipentene (tetrabromide, m. p. 124°); 10 p.c. of *l*-borneol (acid phthalate, m. p. 201 to 202°, conversion to camphor); 10,7 p.c. of cadinene (dihydrochloride, m. p. 117 to 118°).

The oil from the needles of *Pinus palustris* (yield 0,417 p.c.) shewed: $d_{15°}$ 0,8841; α_D — 32,50°; $n_{D15°}$ 1,4834; acid v. 0,67; ester v. 5,91; ester v. after acetylation 40,46. It had the same composition as the oil obtained from leaves and twigs: 2 p.c. *l*-α-pinene; 12 to 13 p.c. *l*-camphene; 50 p.c. *l*-β-pinene; 5 p.c. dipentene; 9,8 p.c. *l*-borneol and 11 p.c. of cadinene.

For the oil from the cones of *Pinus palustris* Schorger established the following properties: $d_{15°}$ 0,8756; $\alpha_{D28°}$ — 9,22°; $n_{D15°}$ 1,4760; acid v. 0,42; ester v. 3,95; ester v. after acetylation 31,07. The composition was as follows: 39,6 p.c. of *d*-α-pinene (nitrolpiperidine, m. p. 118 to 119°); 12 p.c. *l*-camphene (*iso*borneol, m. p. 208 to 210°); 25 p.c. *l*-β-pinene (nopinic acid, m. p. 125 to 126°); about 7 p.c. of dipentene (tetrabromide, m. p. 123 to 124°); 1,4 p.c. *l*-borneol (m. p. 202 to 203°) and about 2 p.c. of cadinene (hydrochloride, m. p. 116 to 117°).

In the oils from *Pinus palustris,* caprylic, capronic and oenanthic acids may possibly be present, esterified with borneol. The presence of dextro-rotatory α-pinene in the oil from the cones of *Pinus palustris* is interesting, as the needles and twigs of this conifer contain *l*-α-pinene.

In a later publication Schorger[1]) describes the oil from needles and twigs, and the one from the bark, of *Abies concolor,* (Gord.) Parry. This conifer is found in the mountainous districts of the western United States. From needles and twigs he obtained an average of 0,128 p. c. of an oil of the following figures: $d_{15°}$ 0,8720 to 0,8777; $\alpha_{D25°}$ — 20,11 to — 27,94°; $n_{D15°}$ 1,4781 to 1,4796; acid v. 1,01; ester v. 12,52 to 27,34; ester v. after acetylation 47,84 to 55,51. The following bodies were found in the oil: furfurol (colour reaction with aniline hydrochloride); 12 p.c. *l*-α-pinene (nitrolpiperidine, m. p. 118,5°); 8 p.c. *l*-camphene (conversion to *iso*borneol); 42 p.c. *l*-β-pinene (nopinic acid, m. p. 126,5 to 127°); 15 p.c. *l*-phellandrene (nitrite, m. p. 102°); 9,5 p.c. *l*-borneol (oxidation to camphor, semicarbazone, m. p. 236 to 237°) and a green oil of the b. p. from 240 to 310°. Borneol also occurs in the oil in the form of its acetate; acetic acid was characterized by its silver salt.

The bark of *Abies concolor* contains 0,095 p. c. of oil ($d_{15°}$ 0,8767 and 0,8702; $\alpha_{D20°}$ — 20,95 and — 20,15°; $n_{D15°}$ 1,4833 and 1,4809; acid v. 1,22 and 0,87; ester v. 6,38 and 6,43; ester v. after acetylation 23,34 and 20,45) the composition of which is as follows: furfurol (colour reaction with aniline hydrochloride); 9 p.c. *l*-α-pinene (nitrolpiperidine, m. p. 118°); 60 p. c. *l*-β-pinene (nopinone semicarbazone, m. p. 188°); about 13 p. c. of dipentene (dihydrochloride, m. p. 49 to 50°; a solid bromide was not obtained) as well as 7 p.c. of a green oil of a boiling point 250 to 300°.

From the needles and twigs of *Pinus ponderosa,* Laws. (western yellow pine) Schorger[2]) obtained 0,04 to 0,126 p.c. of a light yellow to green volatile oil showing: b. p. 161 (ord. pressure) to 185° (35 mm.); $d_{15°}$ 0,8718 to 0,8849; $\alpha_{D20°}$ — 15,73 to — 19,59°; $n_{D15°}$ 1,4789 to 1,4838; acid v. 0,67 to 2,36; ester v. 3,88 to 8,1; ester v. after acetylation 24,11 to 35,68. The oil contained probably about 2 p. c. of *l*-α-pinene (nitrosochloride, m. p. 102,5°) and as principal constituent 75 p. c. of *l*-β-pinene (nopinic acid, m. p. 126°; nopinone semicarbazone, m. p. 188°). There were also found: 6 p. c. of dipentene (tetrabromide, m. p. 124°) and presumably also 7 p. c. borneol (oxidation to camphor; m. p. could not be ascertained owing to smallness of quantity of camphor). The oil contained 3,1 p.c. of a high-boiling green body (b. p. 155 to 185° at 35 mm.): $d_{15°}$ 0,9270; $\alpha_{D26°}$ — 8,39°. Formic and acetic acids (silver salts) were present in the free state as well as in the form of ester.

From the cones of *Pinus ponderosa,* Schorger distilled 0,063 p.c. of a light green oil, of the b. p. of 164 to 290°; $d_{15°}$ 0,8757; $\alpha_{D20°}$ — 11,48°; $n_{D15°}$ 1,4789; acid v. 1,27; ester v. 7,2; ester v. after acetylation 22,41.

Furfurol was present in the lowest-boiling parts (colour reaction with aniline hydrochloride). Of further constituents there were: 6 p.c. *l*-α-pinene (nitrosochloride, m. p. 103°); 60 p.c. *l*-β-pinene (nopinic acid, m. p. 126 to 127°); 12 to 13 p.c. of dipentene (dihydrochloride, m. p. 50°) and the high-boiling green oil found in the oil from the needles.

Furthermore, Schorger describes the oil from the needles and twigs of *Pinus Lambertiana,* Dougl. (sugar pine), the turpentine oil of which he had examined at an earlier date[3]). The yield was 0,045 to 0,120 p.c.; b. p. 158 to 250°; $d_{15°}$ 0,8676 to 0,8738; $\alpha_{D20°}$ — 11,07 to — 16,50°; $n_{D15°}$ 1,4777 to 1,4795; acid v. 0,68 to 2,38; ester v.

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[1]) *Journ. Ind. Eng. Chemistry* **6** (1914), 809. — [2]) *Ibidem* 893. — [3]) Comp. *Report* April **1913**, 101.

2,22 to 5,91; ester v. after acetylation 23,25 to 32,04. The oil contained traces of furfurol (colour reaction), about 20 p. c. of *l*-α-pinene (nitrolpiperidine, m. p. 119°), 51 p. c. *l*-β-pinene (nopinic acid, m. p. 126°; nopinone semicarbazone, m. p. 188,5°), 12 p. c. dipentene (tetrabromide, m. p. 124°; dihydrochloride, m. p. 50°), 8 p.c. *l*-borneol (oxidation to camphor), combined acetic and higher fatty acids, as well as some high-boiling bodies of a green colour.

Schorger also examined the oil from the cones of *Pinus Lambertiana*. It is a light green oil of the b. p. 159,5 to 290°. Yield 0,318 p. c.; $d_{15°}$ 0,8692; $\alpha_{D20°}$ — 23,18°; $n_{D15°}$ 1,4771; acid v. 0,63; ester v. 3,75; ester v. after acetylation 17,04. It contains traces of furfurol (colour reaction), 22 p. c. *l*-α-pinene (nitrolpiperidine, m. p. 116°), 21 p.c. *l*-camphene (conversion to *iso*borneol, m. p. 211 to 212°), 39 to 40 p.c. *l*-β-pinene (nopinic acid, m. p. 126°; nopinone semicarbazone, m. p. 188 to 188,5°), 4 to 5 p.c. dipentene (dihydrochloride, m. p. 49 to 50°) and 1 p.c. of a high-boiling body, possibly a sesquiterpene.

Finally, Schorger[1]) published a paper on the oils from the needles and twigs of *Pinus Sabiniana*, Dougl., *P. contorta*, Loud., and *Abies magnifica*, Murr.

Whereas the turpentine oil from *Pinus Sabiniana* consists in the main of *n*-heptane, the oil obtained from the needles and twigs of this tree (yield of 0,078 to 0,102 p. c.) contains chiefly terpenes, and only 3 p. c. of heptane, recognized by its properties: b. p. 98,5 to 101°; $d_{15°}$ 0,7013. The oil had the following constants: $d_{15°}$ 0,8517 to 0,8566; $\alpha_{D20°}$ — 20,93 to — 38,36°; $n_{D15°}$ 1,4670 to 1,4708; acid v. 1,41 to 2,05; ester v. 6,77 to 11,98; ester v. after acetylation 25,86 to 37,16. The contents are about 59 p. c. of *l*-α-pinene (nitrolpiperidine, m. p. 117°), 18 p. c. *l*-limonene (tetrabromide, m. p. 104°) and about 3 p.c. of a green oil of a b. p. 265 to 290°. In addition, a saponified fraction of the b. p. 206 to 235°, upon oxidation, yielded anisic acid (m. p. 154°), which points to methylchavicol.

The oil from the twigs and needles of *Pinus contorta* (lodgepole pine) was obtained by Schorger to the extent of 0,234 p. c.: $d_{15°}$ 0,8690; α_D — 17,84°; $n_{D15°}$ 1,4831; acid v. 0,9; ester v. after acetylation 32,3. He proved the presence of traces of furfurol (reaction with aniline hydrochloride), about 3 p.c. *l*-α-pinene (nitrolpiperidine, m. p. 118°), about 6 p. c. *l*-camphene (conversion into *iso*borneol, m. p. 205 to 207°), 19 p. c. *l*-phellandrene and dipentene (nitrite, m. p. 102°; dihydrochloride, m. p. 49°) and 7 p. c. cadinene (hydrochloride, m. p. 117 to 118°; hydrochloride rotated to the left, cadinene to the right). A fraction of the b. p. 205 to 235°, when oxidized, yielded an oil smelling strongly of camphor and anisic acid (m. p. 183 to 184°). Presumably borneol and methylchavicol are therefore also present in the oil.

From twigs and needles of *Abies magnifica* (red fir), Schorger obtained 0,154 p.c. of a light green oil of a pungent, unpleasant odour. $d_{15°}$ 0,8665; α_D — 16,70°; $n_{D15°}$ 1,4861; acid v. 0,75; ester v. 9,93; ester v. after acetylation 36,22. There were present: traces of furfurol (aniline hydrochloride reaction); about 18 p.c. of *l*-β-pinene (nopinic acid, m. p. 126 to 127°); 52 p.c. *l*-phellandrene (nitrite, m. p. 102 to 103°); 7,5 p.c. *l*-borneol (oxidation to camphor) and about 13 p.c. of a green oil of a b. p. 255 to 260°.

Some time ago we too were in a position to examine various American pine-needle oils, received from our New York branch office. Unfortunately only small quantities had been placed at our disposal, so that all we could do was to prove the presence of the more important constituents.

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[1]) *Journ. Ind. Eng. Chemistry* **7** (1915), 24.

The needle oil from *Pinus heterophylla* had an odour similar to that of pine-needle oil from *Abies alba*, reminding at the same time of higher fatty aldehydes. We ascertained the following constants: $d_{15°}$ 0,8879; α_D — 35° 23′; $n_{D20°}$ 1,48568; acid v. 0,6; ester v. 10,1; soluble in 7 volumes and more of 90 p.c. alcohol, with turbidity. About 70 p.c. of the oil distilled up to 72° (3 mm.). Treated with neutralized bisulphite solution, the residue formed a small quantity of a solid bisulphite compound which, when distilled with steam in presence of soda solution, produced traces of a semi-solid body, the odour of which reminded distinctly of lauric aldehyde. The semicarbazone remained of paste-like consistence. On account of the small quantity at our disposal it could not be purified. The high-boiling parts, which did not react with bisulphite, smelled like sesquiterpene.

In the fractions which passed over up to 72° (3 mm.) we proved: *l*-α-pinene (b. p. 162°; α_D — 24° 37′; nitrosochloride, m. p. 103 to 104°; nitrolbenzylamine, m. p. 123 to 123,5°), *l*-β-pinene (b. p. 162 to 163°; nopinic acid, m. p. 125 to 126°) and possibly also camphene. On hydrating the hydrocarbons boiling between 162 and 163°, a solid mass was formed, which smelled distinctly of *iso*borneol; through oxidation with Beckmann's mixture we obtained a product smelling like camphor. The quantity was too small to permit of purification.

The needle oil from *Pinus palustris* also resembled the oil of *Abies alba* in odour. $d_{15°}$ 0,8849; α_D — 30° 15′; $n_{D20°}$ 1,48277; acid v. 0,9; ester v. 4,6; soluble in 6 volumes of 90 p.c. alcohol, with slight opalescence. About 57 p.c. of the oil passed over up to 40° (6 mm.). By means of neutralized bisulphite solution, a body was separated from the residue, which smelled of lauric aldehyde. The high-boiling parts of the oil smelled like sesquiterpene. In the fractions of the b. p. 164 to 165° ($d_{15°}$ 0,8701; α_D — 17°) we found *l*-α-pinene (nitrolbenzylamine, m. p. 123 to 124°) and β-pinene (nopinic acid, m. p. 125,5 to 126°). From 18 g. of this fraction we obtained, by single oxidation, 5 g. of a purified sodium nopinate.

Needle oil from *Pinus ponderosa*. This oil, too, resembled the oil from *Abies alba* in odour. It did not react with neutralized bisulphite solution. It had the following properties: $d_{15°}$ 0,8796; α_D — 17° 16′; $n_{D20°}$ 1,48033; acid v. 0,6; ester v. 8,6; soluble in 5,5 volumes and more of 90 p.c. alcohol. About 10 p.c. of the oil boiled between 159 to 164°, producing a small quantity of a nitrosochloride melting at 104°, which points to the presence of α-pinene. About 50 p.c. boiled from 164 to 170° (α_D — 18° 38′) and contained *l*-β-pinene (nopinic acid, m. p. 126 to 126,5°). With a single oxidation 12 g. of this fraction yielded 5 g. of purified sodium nopinate. The fractions boiling above 176° were treated in the usual way with phthalic anhydride, resulting in traces of an alcohol smelling of borneol.

We may add that this oil is obtained on the Pacific coast as a by-product in the manufacture of so-called pine-needle wool (forest wool) *(Lana pini)* which is used in the manufacture of mattresses[1]).

Oil of Ramona stachyoides. On page 107 of our *Report* April **1912** we mentioned a paper by F. Rabak on the oil of the labiata *Ramona stachyoides*. Further particulars on the composition of this oil are found in a publication by C. E. Burke and C. C. Scalione[2]) who distilled the oil from leaves and twigs collected in February, obtaining a yield of 0,9 p.c. Due consideration must be given to the fact that the raw material had slightly

[1]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 132. — [2]) *Journ. Ind. Eng. Chemistry* **6** (1914), 804.

dried in transit. The properties of the oil were: $d_{15°}$ 0,8979; α_D + 24,4°; n_D 1,4729; acid v. 2,2; ester v. 1,6; insoluble in 70 p.c. alcohol. When chilled, no solid parts separated, contrary to the oil examined by Rabak, from which 11,3 p.c. of camphor separated at — 15°. The oil described by Rabak also showed somewhat different constants, *viz.*, $d_{24°}$ 0,9144; α_D + 30,2°; n_D 1,4682; soluble in 1,5 to 3,5 volumes of 70 p.c. alcohol. Burke and Scalione found 6 p.c. α-pinene (m. p. of the hydrochloride 131°), 30 p.c. cineol (phosphoric acid method; identification by the iodol compound), 25 p.c. inactive terpenes, 8 p.c. thujone (b. p. 200°; d 0,917; α 25,9°; tribromide, m. p. 122°), 25 p.c. camphor and 5 p.c. resinified parts. The inactive terpenes possibly consist of dipentene and terpinene. Traces of a solid bromide pointed to the presence of the first-named body, whereas a brownish deposit, which formed when shaking with Beckman's chromic acid mixture, indicated terpinene[1]).

In the oil examined by Rabak there were more high-boiling parts, which might be due to the fact that the raw material had been collected later in the season.

Oil of Ranunculus japonicus. Concerning an oil obtained from the fresh herb of *Ranunculus japonicus* we refer readers to page 79.

Roman Chamomile Oil. On page 64 of this *Report* we have pointed out that, according to Senft, the variety *β-floscula* of *Anthemis nobilis* (a variety without marginal flowerets) is said to be distinguished by its particularly powerful aromatic odour, to which we might here add that some years ago we distilled the mother-plant and its variety separately without, however, being able to trace any difference in odour.

	yield	$d_{15°}$	$n_{D20°}$	acid v.	ester v.	
single flowers with margin	0,33 p.c.	0,9180	1,44891	13,1	242,4	soluble in 1 volume of 80 p.c. alcohol; on more being added, strong separation of paraffin.
„ „ without „	0,3 p.c.	0,9148	1,44741	6,1	255,3	

From double flowers, as found on sale in chemists' shops, we obtained a yield of 1.75 p.c. of an oil showing the following properties: $d_{15°}$ 0,9097; α_D + 1°10′; $n_{D20°}$ 1,44418; acid v. 11,2; ester v. 277,2; soluble in about 6 volumes of 70 p.c. alcohol with fairly considerable separation of paraffin.

On this occasion we might mention an observation we made in the course of the last few years. Whereas, according to the observations recorded in technical literature, slight dextro-rotation is characteristic for Roman chamomile oil (up to + 3°) we have occasionally found slight laevo-rotation in oils of our own distillation. Such an oil had a rotation of α_D — 2° 30′, the other constants being normal: $d_{15°}$ 0,9097; $n_{D20°}$ 1,44642; acid v. 3,8; ester v. 271,7; soluble in about 10 volumes and more of 70 p.c. alcohol, with separation of paraffin. We are of opinion that this laevo-rotation occurs fairly frequently with Roman chamomile oil and that so far it has escaped observation merely because the rotation often cannot be ascertained with certainty owing to the intense coloration of the oil. With the oils in question, determination was only successful owing to the use of the sodium lamp recently constructed by E. Beckmann[2]) which is distinguished by its extraordinary illuminating power. Contrary to ordinary sodium lamps in which a solid sodium compound is evaporated in the flame, the coloration of the flame is here attained by the introduction of salt-dust, produced by electrolysis of a 2 to 4 p.c. solution of sodium hydroxide or sodium

[1]) Comp. von Baeyer, *Berl. Berichte* **27** (1894), 815. — [2]) *Berl. Berichte* **45** (1912), 2523.

carbonate. The illuminating power is greatly intensified if the upper end of the burner tube is surrounded by a tube closed below, into which oxygen is passed, thus enveloping the flame all round in an oxygen zone. A still greater illuminating power is obtained if instead of ordinary coal gas hydrogen is used.

Cultivation experiments with Roman chamomile carried out in Austria are described on page 64.

Rose Oil (Otto of Roses). An American contemporary[1]) discusses the possibility of cultivating roses in Oregon, because its climate and soil are similar to Bulgaria. In the near future a well known Oregon rose expert intends planting an acre in Brooks (Ore.) with rose-plants which he hopes to receive from Bulgaria.

As is well known, the articles most used in the sophistication of otto of roses are mainly palmarosa and geranium oils. In order to cover these additions, according to reports published by N. Petkow[2]), "stereoptene" *(sic!)* or "ceril" (two preparations placed on the market by Swiss firms) have come to be used of late. The so-called stereoptene examined by him had a m.p. of 38,5°; acid v. 2,0; ester v. 3,5; iodine v. 4,6; refractory index (at 50°) 13; it was readily soluble in ether and chloroform, and in-insoluble in alcohol. Ceril had an acid v. of 1,2; ester v. 9,1; iodine v. 174,4, and refractory index (at 40°) 43. Six pure rose oils examined by the author had the following values: $d_{25°}$ 0,8535 to 0,891; α_D — 1,04 to — 2,9°; refractory index at 25°: 43,9 to 51,2; acid v. 1,1 to 1,9; ester v. 8,3 to 10,9; iodine number (5 samples) 170,8 to 189,1; these figures agree approximately with the values found by ourselves in genuine rose oils. He also examined a concrete rose-product, obtained by extraction of rose flowers with light petroleum; it was a yellowish soft mass of an odour like otto of roses and of the following properties: acid v. 7,1; ester v. 31,4; iodine number 51,3; refractory index (at 60°) 62.

Rose Oil, Russian. Roure-Bertrand Fils[3]) give the following figures for a rose oil obtained from Tiflis: $d_{15°}$ 0,8618; α_D — 2° 28'; congealing point + 19°; it contained 23,1 p.c. of stearopten, 0,37 p.c. of free acid (calculated as acetic acid), 2,79 p.c. ester (calculated as rhodinyl acetate), 27,53 p.c. rhodinol (citronellol), 41,44 p.c. geraniol and β-phenylethyl alcohol, besides 4,77 p.c. of terpenes.

Oil of Sage. Some time ago Wallach[4]) found *l*-camphor in an oil from large-leaved sage. At a later date[5]) we published the constants of a Syrian sage oil, which in the opinion of experts originated from *Salvia triloba*, L. In this oil, of which only about 25 g. were at our disposal, we have now been able to prove with certainty *l*-camphor (semicarbazone, m. p. 235 to 236°) and to indicate the presence of thujone as being probable. In a methylalcoholic solution of the camphor slight laevo-rotation was observed. Owing to the small quantity of the fraction of the b. p. 199 to 215° which smelled distinctly of thujone, it was impossible to prove it by a derivative.

About the cultivation of sage plants, see page 64.

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[1]) *Oil, Paint and Drug Reporter* **86** (1914), No. 10, p. 10. — [2]) *Zeitschr. f. öff. Chem.* **20** (1914), 149; *Chem. Zentralbl.* **1914**, I, 2020. — [3]) *Berichte von Roure-Bertrand Fils* April **1914**, 12. See also *ibidem* October **1902**, 24; comp. *Report* October **1907**, 81. — [4]) *Nachr. K. Ges. Wiss.* Göttingen **1905**, Heft 1, 1; *Report* October **1905**, 62. — [5]) *Report* October **1907**, 81.

Sandalwood Oil, East Indian. The Dutch Pharmacopoeia IV stipulates that sandalwood oil should dissolve in 5 volumes of 70 p.c. alcohol, but it indicates 15° as temperature for the observation. In discussing the question (*Report* October **1906**, page 88) we pointed out at the time that the indications should refer to a temperature of 20°, as most sandalwood oils would not pass the test if it were made at a temperature of 15°. M. Baning and P. van der Wielen[1]) have arrived at the same result when examining a number of unadulterated sandalwood oils. They are of opinion that instead of the solubility it would be better to determine the temperature of separation for a mixture of one part by weight of sandalwood oil and 4 parts by weight of 70 p.c. alcohol. This mixture should be clear at 24°, otherwise the oil must be looked upon as adulterated. For example, a sandalwood oil, the separation temperature of which was 17,2°, showed temperatures of 21,8, 24,6 and 29° respectively after additions of 2,13 p.c., 4,26 p.c. and 6,39 p.c. of cedarwood oil. The separation temperatures for mixtures of sandalwood oil with turpentine, light and heavy camphor oils were also determined.

We fail to see any advantage in this proposal, as against the usual way of determining the solubility; in our opinion there is no cause for such an alteration. The solution of normal sandalwood oils requires 3 to 5 volumes of 70 p.c. alcohol. The wording of the pharmacopoeia, as in force hitherto, may well be left as it is, if the test temperature be altered to 20°. If a graduated glass cylinder is used[2]), such a test offers no difficulties whatsoever.

In the *Apotheker Zeitung*, E. Wende[3]) published a method for acetylating sandalwood oil, and saponifying acetylsantalol, the advantages of which are that a chemist may make these tests with the ordinary means at his disposal in his dispensary. Acetylation and saponification are carried out under pressure. The former is carried out in a well-closed glass-stoppered bottle, of about 100 g. capacity in the infusion jar, the saponification in the same manner, in the ordinary water-bath.

As illustrated in a table appended to the paper in question, the results obtained by this method agree well with those obtained according to the instructions given in the Ph. G. V.

In our last *Report* (page 89) we described a few sandalwood oils from Mauritius, sent us by the Imperial Institute of London. About the same oils a report has now made its appearance in a publication of this Institute[4]). The constants laid down show but few and very unimportant divergences, so that we need merely refer to the paper.

Santolina Oil. The ketone santolinenone, which had been found some time back by Francesconi and Scaraffia[5]) in santolina oil (from *Santolina Chamaecyparissus*, L., N. O. *Compositae*) has been examined more closely by L. Francesconi and N. Granata[6]). It was found that the ketone santalinenone consists of two unsaturated ketones $C_{10}H_{16}O$, called α- and β-santolinenone by the authors, and that it contains yet a third, saturated ketone, $C_{10}H_{16}O$, probably of the camphor type. α-Santolinenone is optically inactive but is a racemic body. Proof of this was adduced by splitting α-santolinenone hydroxylaminoxime (m. p. 190°) by means of *d*-camphor sulphonic acid into the optical

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[1]) *Pharm. Weekbl.* **51** (1914), 1467. According to a reprint kindly sent us. — [2]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 567. — [3]) *Apotheker Ztg.* **29** (1914), 541. — [4]) *Bull. Imp. Inst.* **12** (1914), 235. — [5]) Comp. *Report* April **1912**, 113. — [6]) *Gazz. chim. ital.* **44** (1914), II. 150; *Chem. Zentralbl.* **1914**, II. 1439.

antipodes. β-Santolinenone too is inactive and probably racemic. Its hydroxylamino derivative melts at 62°. The third ketone is laevo-rotatory and yields a dextrorotatory oxime of the m. p. 116 to 117°. The ketone can only be regenerated with difficulty by means of acids.

Thujone, which had been suspected by us in santolina oil[1]), could not be ascertained.

Shô-Gyū and Yu-Ju Oils. A tree occurs in many parts of Formosa which, as reported by K. Nagai[2]), shows a great similarity to the camphor tree, but differs from it from a botanical point of view as well as in the composition of the oil. The natives call it *"Gu-Chiu"*. About the botanical position nothing is known. All that is known is that the tree probably belongs to the N. O. of *Lauraceae*. The "black camphor tree" seems to be identical with this tree, but as long as no flowers have been collected and examined, it will hardly be possible to ascertain the botanical name. The leaves of the Shô-Gyū tree are much thicker and of a darker green colour than the camphor leaves. As the leafy branches are frequently so high up that it is difficult to reach them, the easiest way to distinguish the trees is by scraping a little bit of the wood, preferably from the roots; by the odour it is then recognized whether we are in the presence of a camphor or a Shô-Gyū tree. The wood gives a yield of 1,3 to 3 p.c. of oil (the average being 2,5 p.c.). A total yearly production of 600 000 kin would be easily possible. The oil has the following properties: d 0,900 to 1,031; α_D + 7,75 to + 30°; n_D 1,4750 to 1,51302; acid v. 0,1 to 0,96; ester v. 0 to 2,40; ester v. after acetylation 46,6 to 129,4; soluble in 1 to 12,5 volumes of 80 p.c. alcohol. Quite a number of component parts were ascertained, as specified in the following paragraphs.

Formaldehyde, characterized by Rimini's[3]) reaction.

Sabinene. This hydrocarbon was contained in a fraction of the b. p. 163 to 167° and was recognized by oxidation to sabinenic acid (m. p. 57°), and by its conversion to sabina ketone. α-pinene and camphene could not be proved, at least neither a nitrosochloride nor solid *iso*borneol were obtained.

Dipentene. From a fraction of the b. p. 174 to 178° Nagai obtained dipentene tetrabromide, m. p. 123 to 124°.

α- as well as γ-terpinene occur in Shô-Gyū oil and were characterized by oxidation to the erythritol (γ-terpinene) m. p. 236° and to *i*-α,α'-dihydroxy-α-methyl-α'-*iso*propyl-adipic acid (α-terpinene), of the m. p. 188 to 189°.

Linalool. It was impossible to ascertain the presence of this body beyond doubt.

The fraction of the b. p. 207 to 213° contained terpinenol-4, the presence of which was established by conversion to terpinene terpin and 1,2,4-trihydroxyterpane. After oxidation with alkaline permanganate of potassium solution α,α'-dihydroxy-α-methyl-α'-*iso*-propyladipic acid was formed from the trihydroxyterpane, which in its turn was converted in acid solution and by means of permanganate of potassium into ω-dimethyl-acetonylacetone. On boiling with dilute hydrochloric acid trihydroxyterpane formed, besides *p*-cymene and carvenone. Further, the nitrosochloride melted at 111 to 112°, the nitrolpiperidine at 172 to 174°, phenylurethane at 71 to 72°, and naphthylurethane at 105,5 to 106,5°. Terpinenol is present in the oil in fairly large quantities.

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[1]) *Report* October **1911**, 108. — [2]) Investigations of the Shô-Gyū and Yu-Ju oils produced in Formosa. Monopoly Bureau, Government of Formosa. Taihoku 1914. This paper comprising about 50 pages is illustrated with numerous plates of the Shô-Gyū and Yu-Ju trees, as well as with many maps showing the distribution of these trees in the various parts of Formosa. — [3]) Comp. *Chem. Zentralbl.* **1898**, I. 1152.

The attempts to prove camphor and terpineol remained unsuccessful. On the other hand it was possible to establish the presence of geraniol. This alcohol is contained in a fraction of the b. p. 97 to 112° (8 mm.); diphenylurethane, m. p. 80,5°.

Citronellol too occurs in the oil; the silver salt of the acid phthalate melted at 125 to 126°.

Safrole was proved by oxidation to piperonylic acid (m. p. 228°) and eugenol by producing benzoyl eugenol according to Schotten-Baumann's method (m.p. 69°). Perhaps cadinene (colour reaction) is also present in the oil.

Yu-Ju oil is described by Nagai as a product having a great similarity to camphor oil, but differing from it in that it deposits no camphor in solid form. The Yu-Ju tree is so very similar to the camphor tree that it can only be distinguished from the latter by the smell of the wood. It is not known to which botanical genus it belongs. The tree occurs in the southern parts of Formosa, where the native call it *"Jû-chiu"*, the meaning of which is "oil tree". A yearly production of 50 000 to 60 000 kin would be easily possible. Yu-Ju oil has the same physical properties as camphor oil, but its rotation is lower. $d_{13°}$ 0,942 to $d_{16°}$ 0,972; α_D + 18,88 to + 29,85°; $n_{D19°}$ 1,47457 to $n_{D20°}$ 1,47869. The oil contains the following bodies: furfurol (colour reaction with aniline hydrochloride and *p*-toluidine acetate); *d*-α-pinene (nitrosochloride, m. p. 107 to 108°; nitrolpiperidine, m. p. 117 to 118°; nitrosopinene, m. p. 131 to 132°); camphene (conversion to *iso*borneol, m. p. 209°; phenylurethane, m. p. 138°); β-pinene (nopinic acid, m. p. 126 to 127°); cineol (cineol-iodol, m. p. 112°); dipentene (tetrabromide, m.p. 124 to 125°); α-terpineol (nitrosochloride, m.p. 113°; nitrolanilide, m.p. 155 to 156°; phenylurethane, m. p. 113°); safrole (b. p. 233°; $d_{16°}$ 1,106); eugenol (benzoyl eugenol, m. p. 69°) and camphor which was isolated in solid form from a fraction of the b. p. 110 to 112° (17 mm.). The chief constituent of the oil is cineol.

Oil of Solidago nemoralis. The oil of *Solidago nemoralis,* Ait., a composite distributed over a large part of northern America, was described shortly on page 63 *Report* April **1906**. Recently E. R. Miller and M. H. Eskew[1]) have examined it more closely. The oil had been distilled in October from flowering herb, yielding 0,322 p.c. $d^{25°}_{25°}$ 0,8532; α_D — 16,17°; $n_{D18°}$ 17397; soluble in about 4 volumes of 90 p.c., and in about 24 volumes of 70 p.c. alcohol; sap. v. 5,6; sap. v. after acetylation 9,4. The figures found by us previously were: $d_{15°}$ 0,8799; α_D — 23° 10′; ester v. 14,4; ester v. after acetylation 38,2; turbidly soluble in about 7 volumes of 95 p.c. alcohol. Miller and Eskew found about 0,6 p.c. of phenols and, as chief constituent, α-pinene. The pinene showed α_D — 19,37°, from which the authors conclude that it is a mixture of *l*- and *d*-α-pinene. It was characterized by the nitrosochloride and nitrolpiperidine (m. p. 118 to 119°). Neither phellandrene, nor borneol were found, although a camphoraceous odour was noticed in the oxidation of a fraction to be considered for borneol. The test for camphor was unsuccessful, on the other hand salicylic acid was isolated from the oil by shaking with a 3 p.c. caustic potash lye. With ferric chloride solution it gave its colour reaction, and on being treated with methyl alcohol and sulphuric acid it developed the well known odour of methyl salicylate. In the saponification lye acetic acid was contained (silver salt).

Spearmint Oil. Cultivation experiments with spearmint in Austria are mentioned on page 65.

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[1]) *Journ. Americ. chem. Soc.* **36** (1914), 2538.

Spoonwort Oil, see Cochlearia Oil, p. 64.

Tobacco Oil. By heating 300 kilos of Hungarian tobacco of medium quality with an organic solvent, W. Halle and E. Přibram[1]) succeeded in obtaining 140 g. (= 0,047 p.c.) of a yellowish oil of an overpoweringly strong smell of tobacco. It was entirely free from nitrogen, gave an acid reaction with litmus and boiled from 77 to 100° (26 mm.). Although it had been previously shaken with soda solution, it again showed an acid reaction after distillation. By its odour, determination of boiling point and density, titration and analysis of the barium salt this acid was recognized as *iso*valeric acid. In a fraction boiling from 72 to 82° (18 mm.) a hydrocarbon was present, to which possibly the formula $C_{10}H_{18}$ or $C_{11}H_{20}$ may have to be assigned. This hydrocarbon yields as a resolution product an acid which is insoluble in chloroform, and which appears to be identical with terephthalic acid; furthermore an acid soluble in chloroform, presumably *iso*butylacetic acid. Tobacco oil also contains an oxygenous high-boiling fraction.

Turpentine Oil. From our reference on page 95 of our previous *Report* to a paper by W. Steinkopf and M. Freund about the influence of aluminium chloride on turpentine oil, the impression might prevail that C. Engler and his collaborators were the first to study polymerisation of hydrocarbons under the influence of aluminium chloride. In reality this reaction was first described by F. Heusler as far back as 1896[2]).

A. Heiduschka[3]) reports on the bromine heating value of turpentine oil. He mixed 20 cc. of a solution of the turpentine oil to be examined with chloroform in a Weinhold (Dewar) vacuum vessel, ascertained the temperature of the solution, added 1 cc. of bromine and then read off the highest temperature. Considerable differences were found between laevo- and dextro-rotatory turpentine oils. In Heiduschka's opinion this method might be found useful in analyses for purity of turpentine oils, but a considerable number of experimental results will have to be collected first.

Further, a paper by C. Grimaldi and L. Prussia[4]) has to be mentioned, describing the determination of petroleum derivatives and benzene hydrocarbons in turpentine oil by means of mercuric acetate. For this purpose 75 g. of mercuric acetate are placed in a flask with graduated neck, and of 500 cc. capacity, along with 200 cc. of distilled water, 100 cc. glacial acetic and 10 cc. of the oil to be examined. The flask, which is connected with a reflux condenser, is heated for two hours in a water bath of 80° and shaken repeatedly. After cooling it is filled up to zero point with dilute nitric acid. The quantity of unattacked oil may be read off easily. In this treatment pure turpentine oil is oxidized away, inasmuch as it consists chiefly of pinene, which is attacked, forming a dioxypinene[5]). Adulterants, such as petroleum distillates or benzene hydrocarbons, are not attacked, or only in part.

Wherever great correctness is not absolutely necessary, this method is said to be successfully applied. It is more especially useful whenever small quantities only are at the disposal of the analyst, as *f.i.* in the examination of varnish solvents.

The application of this method for the analysis and determination of tar derivatives used in the adulteration of turpentine oil (benzene, xylene, toluene) had not yielded any satisfactory results so far.

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[1]) *Berl. Berichte* **47** (1914), 1394. — [2]) *Zeitschr. f. angew. Chem.* **9** (1896), 292, 318. — [3]) *Chem. Ztg.* **38** (1914), 441. — [4]) *Annal. di Chim. applic.* **1** (1914), 324. — *Chem. Ztg.* **38** (1914), 1001. — [5]) Comp. *Report* April **1903**, 83; April **1904**, 100; October **1906**, 101.

On page 98 of our *Report* April **1913** we discussed a paper by E. Sieburg on the effect of turpentine oil in phosphorus poisoning. Later Sieburg[1]) attempted to decide whether turpentine oil acts as an antidote in phosphorus poisoning, if the phosphorus has already been assimilated. In order to test the supposition that the formation of pinol hypophosphorous acid was the cause of the antidotal effect of turpentine oil, Sieburg made a subcutaneous injection of a fatal dose of phosphorus, in a 0,5 p.c. olive oil solution, in experimental animals; at the same time he tried to neutralize the action of the poison by subcutaneous application of pinene, *i.e.* pinene containing peroxide changed by exposure to the air. No appreciable effect was noticeable, not even when the animals were exposed to an oxygenated atmosphere. Even *in vitro,* when mixing phosphorus with a paste of animal organs and turpentine oil at 40°, it could not be observed that turpentine oil possessed the capacity of combining with phosphorus. It follows that the animal system possesses a greater affinity for phosphorus than the terpenes.

A. W. Schorger[2]) reports on the examination of samples of authentic American turpentine oils. He collected the samples himself in the producing districts, and made careful notes as to the time when the turpentine was obtained, on which day the tree had been tapped and from which district the oil originated. The physical data of all the oils were determined and the boiling behaviour examined. The voluminous material of figures was collected in the form of tables and graphic plates. Generally speaking turpentine oils from "scrape" (scraped-off resin) are specifically heavier than the oils derived from "dip"; oils obtained in spring are heavier than those produced in autumn; furthermore oils derived from the "box" system are heavier than those derived from the "cup and gutter" system, &c. The differences are, however, insignificant. If turpentine oil be suitably stored, its physical properties are not affected within a year, or hardly so. The average values were found to be: $d_{15°}$ 0,8685; $n_{D15°}$ 1,4730; the oil should begin to boil at about 156°.

Turpentine oil from *Pinus Jeffreyi.* According to an investigation by Schorger[3]) on the oleoresins of the *Jeffrey* and the singleleaf pine, the volatile oil from *Pinus Jeffreyi,* A. Murr. consists of about 95 p.c. of *n*-heptane and 5 p.c. of an aldehyde which he believes to be citronellal.

As we were able to obtain a quantity of oleoresin of *Pinus Jeffreyi* through our New York branch, last summer, we had an opportunity of studying the volatile oil of this resin, and of investigating as to whether the aldehyde is really identical with citronellal.

The constants of the oil, obtained from the resin by steam distillation, were as follows: $d_{15°}$ 0,7051; α_D — 0° 10′; $n_{D20°}$ 1,39653; acid v. 0; ester v. 5,2; ester v. after acetylation 8,7; soluble in 5,5 volumes and more of 90 p.c. alcohol. The resin yielded 9,4 p.c. of oil.

The oil was colourless, of a pleasant odour reminding of orange oil, and by far the largest part distilled under ordinary pressure from 96 to 100°. As was also found by Schorger, this fraction consists almost exclusively of heptane.

From the higher-boiling parts of the oil, after repeated distillation, some fractions were separated which smelled distinctly like decylic aldehyde and which soon solidified when shaken with sodium bisulphite liquor. The aldehyde obtained from the double-

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[1]) *Arch. internat. de Pharm. et de Thér.* **14**, 123; *Chem. Zentralbl.* **1914**, II. 65. — [2]) *Journ. Ind. Eng. Chemistry* **6** (1914), 541. — [3]) *Ibidem* **5** (1913), 971; *Report* April **1914**, 96.

compound by separation with soda distilled from 70 to 75° (4 mm.) and its odour did not resemble citronellal at all, but rather *n*-decylic aldehyde. $d_{15°}$ 0,8212; $\alpha_D \pm 0°$.

In order to characterize the aldehyde further use was made of its thiosemicarbazone which was not known so far, but which is easily obtained by heating 1 cc. of the aldehyde with 0,5 g. of thiosemicarbazide and 20 g. acetic acid (80 p.c.) for a short time. This mixture, diluted with a little water, is then allowed to stand for several hours. The thiosemicarbazone, which crystallizes when the solution cools, melts at 99 to 100°. Benzene is best used for recrystallization.

In similar manner the thiosemicarbazones of the following aldehydes were produced: —

	m. p. of the thiosemicarbazones
n-nonylic aldehyde	77°;
n-octylic aldehyde	94 to 95°;
citronellal	54 to 55°.

The aldehyde from the turpentine oil of *Pinus Jeffreyi* cannot therefore be identical with citronellal, but is proved to be *n*-decylic aldehyde. Possibly small quantities of nonylic and octylic aldehydes might also be present in the oil.

The parts left after separating the decylic aldehyde by means of bisulphite liquor smelled of linalool and methylchavicol. B. p. 70 to 75° (4 mm.); $d_{15°}$ 0,9008; $\alpha_D - 10°$.

By means of phenyl*iso*cyanate, linalylphenylurethane, m. p. 66°, was obtained from this fraction. The conjecture that methylchavicol was present besides linalool, was confirmed by an examination after Zeisel, which yielded a strong methoxyl reaction; furthermore, by oxidation with permanganate of potash solution, anisic acid, melting at 180°, was obtained. The quantity available was not, however, sufficient for a more specified proof of methylchavicol.

We have met methylchavicol before now as a constituent of *Pinus* oils; for instance, it was isolated from a wood turpentine oil, the so-called yellow pine oil, and was characterized with certainty by being converted into anethole [1]).

The *Pioneer* of the 1st of May, 1914, prints a paragraph on turpentine production in India, according to which modern machinery of French origin has been erected in Bhawali (United Provinces) for the production of turpentine. A second plant is contemplated for Lahore. The Forest Department considers Indian turpentine production as well capable of being developed to advantage, as the forest areas of the Himalayas are abundantly stocked with *Pinus longifolia* [2]). But the fact should not be lost sight of that, as will be explained further on, the oil is of an inferior quality.

According to Puran Singh [3]) a preliminary estimate has shewn that the only Burmese district, where turpentine production may be carried out to advantage, are the southern Shan States. The possibilities as regards transport will be greatly improved by the completion of a railway line now in course of construction.

Assam turpentine oil does not seem to have any future. The *Pinus Khasya* which occurs in the district forms no extensive forests, the cost of collection is high and, moreover, the oil is not as good as the one obtained in Burmah.

Compared with the forests of *Pinus longifolia*, Roxb., those of *Pinus excelsa*, Wall., are of minor importance, but the oil is excellent and compares favourably with the

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[1]) *Report* April 1910, 106. — [2]) *Nachr. f. Hand., Ind. u. Landw.* 1914, No. 70, p. 4. — [3]) Note on Turpentines of *Pinus Khasya*, *P. Merkusii* and *P. excelsa*; *The Indian Trade Journal* 33 (1914), 293.

best American brands, so that the tapping of *Pinus excelsa* should be encouraged as much as possible. It is hardly probable that turpentine oil from *Pinus longifolia* can take the place of the valuable American kinds, for, as we showed as far back as 1911, the former contains a large percentage of sylvestrene which lacks siccative properties[1]).

It is therefore desirable that the superior oils obtained from *Pinus Khasya*, *P. Merkusii* and *P. excelsa* should be placed on the Indian market.

The rosin of the various Indian, European and American pines showed great similarity. As in the distillation of turpentine from *Pinus longifolia* a fairly high temperature is necessary, the colophony of this kind is somewhat coloured.

For the present turpentine oil produced in India seems to find sufficient demand in the country itself. It is largely used by the railway companies. Under the circumstances exportation to Europe is hardly to be expected in the near future.

So far it had been considered probable that the Japanese part of Saghalin might be looked to in future for the supply of turpentine oil[2]). According to an information published in the *Chemiker-Zeitung*[3]) an excellent turpentine was produced there recently, but the idea of production on a large scale had to be abandoned because the trees that had been tapped for turpentine died already after the third tapping.

About wood turpentine oil a few articles have again appeared which are dealt with in the following paragraphs.

Lunn[4]) deems it unpractical to differentiate between so-called wood turpentines and rosins and gum turpentine and rosins. Wood turpentine oils themselves show very great divergences, according to whether they were obtained by steam distillation of the waste wood, or by dry distillation. The oils obtained in the latter way often possess properties which differ very materially from those of gum turpentine oils. In Lunn's opinion a good gum turpentine oil can be distinguished from a good steam-distilled wood turpentine oil by its odour only. In two oils examined by him the physical properties were practically identical. He found the following values: in a gum turpentine oil: $d_{15,3^\circ}$ 0,866; flash point (Abel cup) 88°, and 97 p.c. consituents boiling below 180°; in a wood turpentine oil obtained by steam-distillation: $d_{15,3^\circ}$ 0,863; flash point (Abel cup) 91°; 95 p.c. of constituents boiling below 180°.

We have also to report upon a paper by M. Adams and C. Hilton[5]) on wood distillation under reduced pressure. The authors consider ordinary dry distillation under reduced pressure, if under close supervision of temperature so as to avoid overheating, the most suitable way for working up waste wood. When experimenting with wood from the western yellow pine *(Pinus ponderosa)* the temperature of the sulphuric acid bath was not more than 5° higher than the temperature in the actual distilling still. At 94° (645 mm.) water passed over and turpentine oil commenced to distil too. The temperature was maintained at 160° for a few hours, the wood becoming brown; above this temperature the material decomposed and at 220° gases made their appearance as decomposition products. In an apparatus specially built for the purpose, a description of which, along with an illustration, is given in the original treatise, the authors carried out an experiment with larger quantities of the raw material. By their examinations they believe to have proved that the pines occurring in the western

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[1]) Comp. *Report* April **1911**, 116; October **1911**, 93. — [2]) Comp. *Report* April **1913**, 104. — [3]) *Chem. Ztg.* **38** (1914), 1054. — [4]) *Oil, Paint and Drug Reporter* **85** (1914), No. 16, p. 36. — [5]) *Journ. Ind. Eng. Chemistry* **6** (1914), 378.

parts of the United States contain sufficient turpentine to make distillation an advantageous proposition. Under favourable circumstances a cord (4000 lbs.) of yellow pine wood yields 25 gallons of wood turpentine oil.

In a detailed publication M. C. Whitaker and J. S. Bates[1]) report on the chemical exploitation of southern pine waste. Most of the waste wood comes from the longleaf southern pine (*Pinus palustris,* Mill.), which tree supplies more than one quarter of the timber used in the United States. The most important parts of *Pinus palustris* are its gum and the wood itself. The yield in gum is rather variable, but its composition is fairly constant. It contains about 20 p.c. of volatile oil (crude turps) which yields from 60 to 80 p.c. of turpentine oil and from 20 to 40 p.c. of heavier oils. The latter are called by the collective name of pine oil.

One tree will supply about 35 p.c. of saw dust, waste wood, &c. Slabs, *i.e.* waste wood with its bark, are to be had in large quantities and are a convenient raw material.

In their experiments the authors treated waste wood (in the form of chips) with diluted alkalis and steam, in order to obtain the rosin and the turpentine oil. In this process they studied the influence of disintegration of the wood, and also considered many other factors which would carry us too far to mention here. The turpentine oil produced by them is free from the unpleasant by-odour of the oils obtained by dry distillation.

The further working-up of the wood according to the various methods tried by the authors need not be mentioned in this *Report,* as in the course of said treatment no more volatile oil was obtained.

Finally we may allude to a paper by M. Toch[2]) on the chemistry of pine oil. As was mentioned above, the heavy oil is meant which is obtained in the fractionated distillation of wood turpentine oil produced by steam distillation. The density of the above-mentioned oil is: $d_{15,5^\circ}$ 0,9291 to 0,9583.

According to A. Hellström[3]) the yield of pure turpentine oil in the pulp factories which work up saw mill waste (about 70 p.c. of pine and 30 p.c. of fir cuttings, &c.) amounts to about 5 kilos per ton of cellulose. If, after separating the turpentine oil, the condensation product of the digestors is worked up for methyl alcohol after Bergström's process, a little more turpentine, contained in the condensation-product in the form of an emulsion is obtained, which is given as amounting to 0,54 kilo of pure turpentine oil per ton of cellulose. The older the sulphate turpentines are, the more are the badly smelling parts condensed and oxidized. Such oils may be separated from the resinous parts by distillation, and easily purified with sulphuric acid.

On a previous occasion[4]) we pointed out that products such as the above-named should not be called turpentine oils. The designation "turpentine oil" must be reserved for the distillate derived from steam-distillation of gum turpentine. According to P. Klason[5]) the essential oil obtained in the digestor at the termination of the process of manufacturing sulphite cellulose consists of about 95 p.c. of cymene.

A waste product collected when blowing off the digestors in the manufacture of wood-pulp from spruce-pine wood, is described on page 83 of this *Report.*

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[1]) *Journ. Ind. Eng. Chemistry* **6** (1914), 289. — [2]) *Journ. Soc. chem. Ind.* **33** (1914), 576. — *Journ. Ind. Eng. Chemistry* **6** (1914), 720. — [3]) *Papierfabrikant* **12** (1914), 1025; *Zeitschr. f. angew. Chem.* **28**, II. (1915), 47. — [4]) *Report* April **1905**, 80; October **1905**, 67, 69. — [5]) Comp. *Report* April **1901**, 67.

Vetiver Oil. In our *Report* October **1912** (p. 112) we mentioned a vetiver oil, described by the Imperial Institute in London, which had been distilled in the Fiji islands. On a further oil of the same origin the April/June *Bulletin* of the above-named Institute[1]) gives the following particulars. The oil was of great viscosity and of the characteristic vetiver odour. It had a yellowish-brown colour which turned into dark green after a little while under the influence of air and light. $d_{15°}$ 1,018; sap. v. 47; soluble in $1^1/_3$ volume of 80 p.c. alcohol; from 3 volumes upward turbidity sets in. As is correctly remarked, it is difficult to give an opinion on the commercial value of such an oil, because *i. a.* the value depends to some extent on the law of supply and demand. The price suggested by divers experts varied between 16/– and 30/– per lb.

In an oil sent us some time back by the Imperial Institute, and which was very likely identical with the above-mentioned sample, we ascertained the following values: $d_{15°}$ 1,0164; $n_{D20°}$ 1,52058; acid v. 31,1; ester v. 17,3; ester v. after acetylation 143,7; soluble in 1 volume of 80 p.c. alcohol, from 2 volumes upwards turbidity set in.

At the same time we may mention a vetiver oil from Indian root, which had been submitted to us by the Imperial Institute some considerable time ago. In its constants it resembles partly the oil distilled in Germany, partly the one produced in Réunion, but differs from both in its rotation which is surprisingly low for a vetiver oil. This is probably due to its unscientific manufacture. This latter point might also explain the extraordinarily small yield (0,26 p.c.), for in an experimental distillation of the raw material sent us at the same time we found double the yield (0,5 to 0,6 p.c.), which, however, is still too small, seeing that normal vetiver root yields from 1 to 3 p.c. of oil. The quantity of oil obtained by us was too small to permit of any constants being determined, we have therefore to confine ourselves to giving the figures for the sample sent us by the Imperial Institute: $d_{15°}$ 1,0052; $\alpha_D + 15° 25'$; $n_{D20°}$ 1,51880; acid v. 29,6; ester v. 12,5; ester v. after acetylation 141,2; soluble in 1,5 volume and more of 80 p.c. alcohol.

Some Seychelles distillates[2]), of which we received samples, were of similar nature, their figures moving within the following limits: $d_{15°}$ 0,9863 to 0,9977; $\alpha_D + 10° 50'$ to $+ 19° 25'$; $n_{D20°}$ 1,52253 (single test); acid v. 8,2 to 16,3; ester v. 10,7 to 17,2; ester v. after acetylation 103,3 to 130,5. Two of the samples dissolved only in 90 p.c. alcohol (about 0,5 volume and more), whereas three others gave a clear solution in 1,5 volume of 80 p.c. alcohol, but from 3 volumes upwards turbidity set in, and on further dilution there was pronounced opalescence. The odour of these oils was similar to the Réunion distillates.

From roots obtained from the Philippine Islands Roure-Bertrand Fils[3]) distilled 0,92 p.c. of an oil of the following properties: $d_{15°}$ 1,0139; $\alpha_D + 30° 8'$; acid v. 21,5; ester v. 6,5; ester v. after acetylation 165,2; soluble in 0,75 volume and more of 80 p.c. alcohol. The oil had a lasting and fine odour.

Wormwood Oil. We gather from the report of Roure-Bertrand Fils (April **1914**, 87) that Auguet (*Annal. des Falsificat.* **6**, 385) has been engaged in the determination of the essential oils in absinth and similar liqueurs, and has also examined alcoholic essences according to the method prescribed in France, which is a modification of the directions as laid down by Sanglé-Ferrière and Cuniasse[4]). It is based on the determination of the iodine absorption by alcoholic solutions of volatile oils, using

[1]) *Bull. Imp. Inst.* **12** (1914), 225. — [2]) *Re* Seychelles vetiver oils compare also *Report* October **1912**, 113. — [3]) *Berichte von Roure-Bertrand Fils* April **1914**, 11. — [4]) *Annal. Chim. anal. appl.* **8** (1903), 17.

Hübl's iodine solution. The latter should be strongly acid, it ought to contain *f. i.* 7,5 to 10 g. hydrogen iodide per litre, and the work should be done at a temperature of 18°. No exact results are obtained in this case with Wijs's iodine solution.

On the cultivation of wormwood in Austria see page 64.

Wormseed Oil, American. On account of the unpleasant taste of American wormseed oil the following form of prescription is recommended in the *Pharmazeutische Zeitung* [**59** (1914), 928]: a mixture of 3 parts of wormseed oil and 30 parts of castor oil is worked in the usual way into an emulsion of 100 parts, to which small quantities of saccharin, peppermint oil, lemon oil, Ceylon cinnamon oil and ethyl acetate are added.

About further prescriptions for making up this remedy compare *Reports* October **1906**, 82; October **1907**, 99; October **1910**, 143 and April **1914**, 99/100.

In No. 224 of the *Public Health Reports* of October 2nd, 1914 (Washington), M. G. Motter advocates the use of American wormseed oil in the treatment of hookworm disease, a treatment about which we had occasion to report some time ago[1]). Thymol, which had formerly been used in fighting this disease, is very difficult to obtain in America in consequence of the war. The author produces nothing new in respect of the use of the oil.

The resolution of *i*-ascaridolic acid into its optical components is discussed on page 107 of this *Report*.

Ylang-Ylang Oil. On page 135 of our *Report* November **1908** we mentioned two ylang-ylang oils obtained from the Seychelles, which had been described by the Imperial Institute of London. Meantime, this Institute[2]) has received two further ylang distillates from the same place, one of which owing to its constants must be classed among cananga oils, whereas the other shows the characteristic ylang oil values:—

1) $d_{15°}$ 0,9200; $\alpha_{D21°}$ — 30°; acid v. 4,2; ester v. 42,2; it yields a clear solution in an equal volume of 90 p.c. alcohol. On further addition of the solvent turbidity sets in.
2) $d_{15°}$ 0,9567; $\alpha_{D20°}$ — 28° 5′; acid v. 3,3; ester v. 126,0; ester v. after acetylation 181; soluble in 90 p.c. alcohol up to 0,8 volume, beyond which point turbidity sets in.

As is specially pointed out, even the second oil cannot compare with a good Manila distillate, as the odour was hardly pleasant and rather pungent.

After a lapse of over 3 years the constants of sample No. 1 were once more determined, when slight increases in specific gravity and in the ester value were observed: $d_{15°}$ 0,9250; $\alpha_{D21°}$ — 28° 36′; acid v. 2,6; ester v. 53,5; soluble in 1/3 volume of 90 p.c. alcohol. From 1 volume upward turbidity set in.

In the same publication[3]) an ylang-ylang oil from the island of Mauritius is mentioned, to which we already referred in our last *Report* (page 101). The values found by the Imperial Institute differ somewhat from those given by ourselves: $d_{15°}$ 0,9883; $\alpha_{D20°}$ — 30°; acid v. 7; ester v. 173, ester v. after acetylation 211; soluble in 0,1 to 2,5 volumes of 90 p.c. alcohol, on further addition turbidity sets in. English experts valued the oil at 3/- to 4/- per oz.

Concerning **Yu-Ju Oil** see page 42 of this *Report*.

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[1]) Comp. *i.a. Report* October **1913**, 108. — [2]) *Bull. Imp. Inst.* **12** (1914), 230. — [3]) *Ibidem* 230.

Novelties.

Copalillo Oil. From Mexico we received a sample of an oil called copalillo oil, as well as a sample of the wood from which it was said to have been distilled. *Exothea Copalillo,* Radlk. (N. O. *Sapindaceae*) will probably have to be considered as mother-plant, at any rate the anatomical structure of the wood points to this family. The constants of the oil were as follows: $d_{15°}$ 0,8504; $\alpha_D + 0° 50'$; acid v. 10,2; ester v. 13,1; soluble in 0,5 volume and more of 90 p. c. alcohol. It was of brownish yellow colour and its odour reminded of linaloe oil, but any considerable content of linalool is out of the question, seeing that the solubility of the oil was far too bad for such a supposition. Unfortunately, a closer examination was impossible owing to insufficient material. We are unable, therefore, to give further particulars about the composition of the oil.

Oil from Doz-herb. Under the designation *"Doz"* we received a herb from Bombay, the botanical examination of which showed it to be a variety of *Artemisia maritima,* L. (N. O. *Compositae*), but this could not be definitely established, as there was not a single blossom to go by. An experimental distillation yielded 0,24 p. c. of a dark green oil of a peculiar, though hardly pronounced odour. The following constants were determined: $d_{15°}$ 0,9696; acid v. 1,8; ester v. 4,2; soluble in about 3 volumes of 70 p. c. alcohol, with separation of paraffin. On account of the dark colour of the oil its rotation could not be ascertained, neither could we examine the oil more closely, as but a few grams were at our disposal.

Oils from Hernandia peltata. Under the designation of "faux camphrier" (spurious camphor tree) we had received, several years ago, a sample of wood, originating from Madagascar, on the oil of which we had published a short note in our *Report* October **1910** (p. 146). As principal constituent it contained a strongly dextrorotatory aldehyde of cumin-like odour. F. W. Semmler and B. Zaar[1]), at whose disposal we had placed a sample of the oil, found that they had to deal with a dihydrocuminaldehyde ($C_{10}H_{14}O$), the laevo-rotatory modification of which they had established at the time in the oil from *Perilla nankinensis,* Desc., also supplied by us, and which was designated by them accordingly perillaldehyde[2]). Furthermore, myrtenal, cineol and d-limonene were found in the oil of "faux camphrier".

Meantime we received samples of the same wood from other quarters. In one instance the article was called *"Bois de Cass"*, in the other instance *"Hazamalanga wood"*. In both cases Madagascar was given as origin. So far all our endeavors to ascertain the botanical origin of this interesting wood, which is used in Madagascar as building timber defying white ants, had always proved in vain. At long last we succeeded in obtaining further parts of the plant in question, thus enabling us to solve the botanical question successfully. Dr. Giessler, custodian of the Botanical Institute of the University of Leipzig, established as mother-plant *Hernandia peltata,* Meissn., N. O. *Hernandiaceae.*

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[1]) *Berl. Berichte* **44** (1911), 815; *Report* October **1911**, 28. — [2]) *Berl. Berichte* **44** (1911), 52; *Report* April **1911**, 93. Comp. also *Report* October **1910**, 146.

Besides wood from the trunk, we have now been able to distil roots, as well as fruits, and have come to the following results: Four samples of trunk wood yielded between 1,03 and 2,06 p. c. of oil of the following values: $d_{15°}$ 0,958 to 0,963; α_D + 83° 45′ to + 104° 12′; $n_{D20°}$ 1,49695 to 1,50111; soluble in 2,5 to 4 volumes and more of 70 p. c. alcohol, in one instance with slight opalescence. Quantitatively the aldehydes of these, as well as of the other oils, did not react with sodium hydrogen sulphite, but they did with neutral sulphite; in this manner between 75 and 80 p. c. of aldehydes were found. The acid v., determined in one oil only, was 4,4; ester v. 47,1.

Wood from the roots yielded 0,5 p. c. of oil of the following properties: $d_{15°}$ 0,9667; α_D + 126° 15′; $n_{D20°}$ 1,50383; aldehyde percentage (sulphite method) 92,5 p. c.; soluble in 2,5 volumes and more of 70 p. c. alcohol.

The distillate obtained from whole fruits (yield 0,5 p. c.) showed the following figures: $d_{15°}$ 0,9528; α_D + 50° 16′; $n_{D20°}$ 1,49554; aldehyde content (sulphite method) 49 p. c. It only dissolved in 0,3 volume and more of 90 p. c. alcohol. Of 80 p. c. alcohol not even 10 volumes sufficed to produce solution.

The almond-shaped kernels contained considerably more oil, namely 1,38 p. c.: $d_{15°}$ 1,0044; α_D + 87°; $n_{D20°}$ 1,50614; acid v. 7,3; ester v. 110,4; not completely soluble in 10 volumes of 70 p. c. alcohol; soluble in 0,5 volume of 80 p. c. alcohol. On more being added, opalescence set in.

All these oils were of light to dark yellow colour and, with the exception of the oil from the fruits, had the characteristic odour of perillaldehyde.

Himalaya cedar Oil. Some time ago, the Forest Research Institute and College in Dehra Dun sent us an oil called Deodar oil for valuation. This oil had been obtained by distillation with steam from the saw-dust of the Himalaya cedar *[Cedrus Deodara* (Roxb.), Loud., *C. Libani*, Barrel. var. *Deodara]*. It possessed a light brown colour and a pleasant, balsamic odour. A close examination gave the following results: $d_{15°}$ 0,9530; α_D + 53° 8′; $n_{D20°}$ 1,51565; acid. v. 2,9; ester v. 14,9; ester v. after acetylation 39,2; not completely soluble in 10 volumes of 90 p. c. alcohol, soluble in every proportion of 95 p. c. alcohol. Under a pressure of 760 mm, 87 p. c. of the oil passed over between 258 to 295°. The first fractions of the distillate (258 to 265°, 14 p. c.) contained a body which yielded a semicarbazone of the m. p. 158°, and which is perhaps identical with the ketone[1]) found in Atlas cedar oil. But the largest part of the oil consists of sesquiterpene, about the identity of which we have not ascertained anything further as yet. A test for cadinene yielded no positive result.

The wood of the Himalaya cedar is largely used in India for building purposes as well as for the manufacture of railway sleepers.

Oil from Libocedrus decurrens. Some time ago our branch house in New York sent us an oil from the needles of *Libocedrus decurrens*, Torr., a conifer occurring chiefly in California[2]). Its odour reminds of savin oil. $d_{15°}$ 0,8756; α_D — 0° 51′; $n_{D20°}$ 1,47544; acid v. 0,9; ester v. 4,6; soluble in 7 volumes of 90 p. c. alcohol and more, with turbidity. 22 p. c. of the oil boiled from 158 to 160° ($d_{15°}$ 0,8640; α_D — 18° 40′) and contained l-α-pinene (nitrolbenzylamine, m. p. 124°). When trying to prove β-pinene in the fractions of b. p. 60 to 67,5° (16 mm) by oxidation to nopinic acid, an acid melting at about 103°

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[1]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 135. — [2]) Comp. J. W. Harsberger, *Phytogeographic survey of North America*. Leipzig, New York 1911, p. 176 (vol. 13 of the work *Die Vegetation der Erde*).

was found. A similar result was obtained by Enklaar when oxidizing a fraction of Dutch myrtle oil[1]), when an acid formed of the m. p. 102 to 103°, which in his opinion may possibly have consisted of i-pinonic acid or impure l-nopinic acid. Another explanation for the formation of the acid would be that in the oil examined by Enklaar, as well as in the one examined by us, a hydrocarbon is present which, when oxidized, yields the acid of the m. p. 103°.

The higher-boiling fractions (b. p. 45 to 72° at 3 mm) resembled carvone in odour, but yielded no semicarbazone.

Oil from Melaleuca hypericifolia. In the Biological Agricultural Institute of Amani (German East Africa) an oil was obtained from the leaves of *Melaleuca hypericifolia*, Sm., a sample of which was submitted to us for valuation. It was of pale green colour and in odour as well as in its constants it showed a certain similarity to the oil of *Eucalyptus Globulus;* $d_{15°}$ 0,9145; α_D + 0° 18′; $n_{D20°}$ 1,46271; soluble in 2,5 volumes and more of 70 p. c. alcohol. The eucalyptol percentage (resorcinol method, separated off in the form of a solid resorcinol combination) amounted to 72 p. c.

Oils from Melaleuca leucadendron var. Two distillates produced in Amani from the leaves of varieties of *Melaleuca leucadendron*, the mother-plant of cajuput oil, were quite different from this latter oil, as was shown by their constants and more especially by their odour. One of these oils originated from the narrow-leaved, the other from the broad-leaved variety. Whereas in cajuput oil proper eucalyptol is the most important part from the point of view of odour, this body is entirely absent from the oil of the broad-leaved variety, and in the oil from the narrow-leaved variety it occurs only in a subordinate position. A further examination showed the oil of the broad-leaved variety to consist of about 78 p. c. of methyleugenol (veratric acid, m. p. 179,5°), *i. e.* of a body which does not occur at all in real cajuput oil. To judge from the basil-like odour of this oil, methylchavicol might be suspected, but a test in this direction gave a negative result. We have not yet examined the oil of the narrow-leaved variety more closely, but we may say at once that it is also of quite a different composition to cajuput oil. We cannot venture an opinion as to how these differences are to be explained.

The constants of the two distillates will be found in the following table:—

	Broad-leaved variety	Narrow-leaved variety
$d_{15°}$	1,0019	0,9056
α_D	— 3° 44′	— 0° 22′
$n_{D20°}$	1,52500	1,47936
acid value	0,4	0,7
ester value	7,6	11,8
ester v. after acetylation	15,2	84,8
soluble in	0,6 volume and more of 80 p. c. alcohol.	1,5 volumes

Oil of Mother-cloves (Anthophylli). As will be known, the berry-like fruits collected from the clove-trees shortly before maturity are called mother-cloves. In an experimental distillation we obtained from this material 2,03 p. c. of an oil of a

[1]) Comp. *Report* October **1912**, 54.

brown colour and of an odour similar to, but weaker than, clove oil. The following constants were established: $d_{15°}$ 1,0933; α_D — 3° 11′; $n_{D20°}$ 1,54332; phenol percentage (ascertained with 3 p.c. caustic soda solution) 88 p.c.; soluble in 1,8 volume and more of 70 p.c. alcohol. Compared with clove oil, the specific gravity its remarkably high, for it exceeds even that of eugenol ($d_{15°}$ 1,071 to 1,074). This was even more pronounced with the specific gravity of the separated phenols, which was 1,1210 (15°). The reason for this phenomenon is to be found in the fact that the phenols consist of only 60 p.c. of eugenol, the balance being made up of a solid combination. Calculated on the original oil its content of this latter body amounts to about 35 p.c. and to about 53 p.c. of eugenol.

The solid phenol has a weak, paraffin-like odour and is almost insoluble in water, but it dissolves more or less readily in organic solvents, as well as in alkali liquor. From alcohol it crystallizes in fine, bold crystals of a m. p. 44 to 45,5°. At 754 mm. it boils between 309 and 310° and at 4 mm. from 146 to 149°. The rotation was found to be ± 0°, the specific gravity in the melted state at 15° was 1,188. A strong reaction was obtained, with benzoyl chloride, the benzoyl combination, after repeated recrystallization from alcohol, melting at 87 to 88°.

Yama-nikkei bark Oil. An oil obtained by us from *Yama-nikkei* bark (wild cinnamon bark; N. O. *Lauraceae*) showed the following constants: $d_{15°}$ 0,9245; α_D + 8° 34′; $n_{D20°}$ 1,47779; acid v. 0,6; ester v. 14,8; soluble in 1 volume and more of 80 p. c. alcohol. The yield was from 1,77 to 2,1 p.c.

The oil was of a light yellow colour and smelled strongly of camphor, with a somewhat ginger-like by-odour. The bulk distilled from 75 to 95° (6 mm.) and solidified in the cold to a camphor paste, from which camphor was obtained, and purified by sublimation; m. p. 175°. With semicarbazide this camphor yielded a semicarbazone of the m. p. 236°; a 25 p.c. solution in chloroform showed a slight optical rotation, *viz.*, — 0° 10′ in a 20 mm. tube. Judging from its odour the fraction obtained at the commencement of the distillation, from 40 to 75° (6 mm.), appears to contain terpenes and cymene; the bark originated from Japan.

Chemical Preparations and Drugs.

Anisole. One of the most powerful remedies against the lice pest among the soldiers at the front (see also page 74 of this *Report*) is, as was only recently discovered, anisole, *i.e.* the methyl ether of phenol (carbolic acid), $C_6H_5 \cdot OCH_3$. It owes its name to the former method of obtaining it from anisic acid, a process which has long been replaced by a more convenient and cheaper one.

As could be read in the newspapers, the discovery of the excellent action of anisole is due to a mere chance. When Prof. S. Fränkel, in Spiegler's Institute for the investigation of cancer (Vienna), was trying experimentally the efficiency of the various remedies recommended against vermin, he asked his assistant to give him the bottle containing aniseed oil (Anis*öl*), and the man fetched anis*ole* by mistake.

We have started the manufacture of this preparation.

Benzoin. Siam benzoin occurs in commerce in loose pieces, which are always purely white and opaque; only on the surface there is a very thin yellow or reddish yellow, transparent film. This film forms only after long storage and is an oxidation product of the resinous mass proper. In order to prove this, F. Reinitzer[1]) exposed benzoin to the air at a warm temperature, and after several weeks a reddish yellow film had covered the originally white surface. On the other hand pieces of benzoin which had been kept for several weeks at a temperature of between 45 and 47° in tubes filled with carbonic acid, remained purely white. Generally speaking, benzoin, according to Reinitzer, oxidizes rather easily.

On this account the resinotannyl benzoate described by Lüdy is no original component of benzoin, but has formed by oxidation of benzoin with the excess of alkali during the process of heating for several weeks. Reinitzer found in Siam benzoin a new colourless, crystallizing substance, lubanyl benzoate[2]). In addition, he was able to prove that benzoresinol does not occur in benzoin in combination with benzoic acid, as presumed by Lüdy, but as a free alcohol.

The benzoresinol contained in Siam benzoin does not agree in all its properties with the benzoresinol obtained by Lüdy from Sumatra benzoin, and therefore Reinitzer called it siaresinol. In order to get lubanyl benzoate, benzoin, freed from the yellow film, is dissolved in ether, to which solution light petroleum is added cautiously. At first only amorphous substances will be precipitated, but later on likewise lubanyl benzoate as minute crystals.

Benzyl alcohol. In an earlier Report[3]) we have mentioned that according to P. Mayer liquid terpineol is a useful medium for microscopic purposes, which in many of its properties is superior to clove oil or eugenol. The same author has quite recently described another entirely new application of benzyl alcohol in microscopic

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[1]) *Arch. der Pharm.* **252** (1914), 341. — [2]) Lubanol from *Luban djawi*, the original name of benzoin. — [3]) *Report* October **1910**, 153.

technics, in a book written by him on microscopy[1]). It is used merely as a medium, mixes clearly on the one hand already with 90 p.c. alcohol, but on the other hand, as regards resins, only with euparal[2]) and gum turpentine, not with Canada balsam. It does not dissolve paraffine wax and celloidine.

An instance for the use of benzyl alcohol in microscopic technics is to be found in a description, published by H. Ambronn[3]), of an experiment to demonstrate Abbe's theory of microscopic perception. He found that benzyl alcohol and a certain kind of cinnamon oil are the best mediums for the immersion of the fibre of the inner bark of the ramie plant, as their exponents of refraction tally almost with those acting in the longitudinal direction of the fibre. The exponent of refraction of benzyl alcohol was 1,540; that of cinnamon oil, 1,597. As the latter value lies between those found for pure Ceylon cinnamon oil and pure cassia oil, Ambronn presumes that the oil he used was perhaps a mixture of the two. In any case, it is easy to make a mixture of the two oils that has the desired refractive power. The difference between the two figures indicates at the same time the intensity of the double refraction, *i. e.* 0,057. This figure agrees very well with the estimations carried out nearly 25 years ago by V. von Ebner with similar fibre in a totally different way, by determining the differences of the phases and of the thickness of the membrane.

Concerning an inferior **artificial Bergamot oil,** we have reported on page 18.

Copaiba Balsam. According to E. Deussen[4]), the determination of the acid and saponification numbers is only of secondary importance for the estimation of officinal copaiba balsam. The determination of its solubility in chloroform, absolute alcohol and light petroleum may serve as a criterion. However, the most important part of the work is the distillation of the balsam with steam for testing the essential oil thus obtained. The optical rotation of the oil must be determined. The limits for the α_D of the oil of Maracaibo balsam are between $-2{,}5$ and $-14°$. It may be advisable at times to make Turner's colour test with the modifications indicated by Deussen and Eger[5]) and, should the result be doubtful, to split the oil up into 3 or more parts by fractionated distillation *in vacuo*. The residue in the vacuum still should likewise be tested in the same manner.

Deussen analysed, under the considerations exposed above, 12 samples of officinal copaiba balsam, bought in the retail trade. He determined the density of these samples, the α_D of the volatile oil, the α_D of the resinous residue and further investigated the several fractions as well as the distillation residue. He gave his results in the form of tables. It was found that 5 of the 12 samples were adulterated with either gurjun balsam or gurjun balsam oil, whereas two others proved to be pure gurjun balsams. Only with the two last, Turner's colour reaction, as indicated in the German Pharmacopoeia V gave no result. Three balsams had been adulterated in another way, as the volatile oil was dextro-rotatory. In order to establish whether there is any adulteration with illurin balsam, the essential oil is split up into about 4 fractions, and their rotatory power determined. Illurin balsam oil yields on simple, not repeated fractionated distillation only dextro-rotatory components.

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[1]) *Einführung in die Mikroskopie*, Berlin, 1914, p. 183. — [2]) A mixture, the composition of which is not exactly known, but which among other substances contains eucalyptus oil and paraldehyde. — [3]) *Zeitschr. f. wissensch. Mikrosk. u. mikroskop. Techn.* **30** (1913), 289. As per a special copy kindly sent us. — [4]) *Arch. der Pharm.* **252** (1914), 590. — [5]) *Chem. Ztg.* **36** (1912), 561; *Report* October **1912**, 49.

A treatise by Deussen on copaiba balsams and their adulteration has been dealt with on page 67 of this *Report*.

Copaiba balsams of different origin have been described on pages 14 and 15 of this *Report*.

Coumarin. In order to study the influence of light on coumarin in the presence of oxygen, G. Ciamician and P. Silber[1]) exposed coumarin to the light from April to November in a spacious vessel and in the presence of water. A sort of brown emulsion had formed during the exposure. The following products of reaction were found: salicylaldehyde, dihydrodicoumarin (m. p. 258°), salicylic acid and a substance which crystallized in long needles and melted at 163°. Dihydrodicoumarin had formed in predominating quantity. In previous experiments of exposing coumarin to the light, carried out in the absence of oxygen, far less dihydrodicoumarin had formed.

Eucalyptol. Concerning a method of titration for determining eucalyptol see page 23.

Eugenol. We have mentioned on page 102 of this *Report* that the test of eugenol for carbolic acid, prescribed by the Austrian Pharmacopoeia, often leads to erroneous conclusions.

Hardwickia Balsam. In summer 1914, we received from the Imperial Institute in London a balsam of *Hardwickia pinnata,* Roxb. (N. O. *Leguminosae*). We have frequently dealt with similar balsams in our *Reports*[2]). The product in question was, like the former, a thick liquid of reddish brown colour, in a very thin layer greenish. The smell was feeble and not very agreeable. It showed the following values: $d_{15°}$ 1,0222; sap. v. 104,0; ester v. 32,6. On distilling the balsam with steam, about 35 p.c. of a colourless oil could be obtained which had a weak odour and showed the following constants: $d_{15°}$ 0,9080; α_D — 6° 7′; $n_{D20°}$ 1,50026; sap. v. 0,3; ester v. 3,9; soluble in 5,5 vols. and more 95 p.c. alcohol with a minimal opalescence.

The rosin, left as a residue after distillation, was brittle and of the colour of the balsam itself; the acid v. was 160,6.

Peru Balsam. L. Rosenthaler[3]) tried to distinguish genuine Peru balsam from the artificial product by determining the optical rotation of its cinnamein. He ascertained **1)** the rotation of the ethereal solution, by mixing 10 g. of Peru balsam with 10 g. of sodium hydroxide solution and 10 g. of water and shaking the mixture afterwards with 50 g. of ether; **2)** the specific rotation of the cinnamein in alcoholic solution, by distilling off the ether from the solution before mentioned, dissolving the weighed residue in about 4 times its quantity of alcohol and determining the density and rotation of this solution. The sap. v., percentage of cinnamein, as well as the sap. v. of this cinnamein, were likewise established for the balsams tested as described.

Generally speaking, a rotation to the right ($[\alpha]_D$ + 0,10 to + 1,13°)[4]) was observed in the etheral and alcoholic solutions of most of the balsams. It is difficult to judge

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[1]) *Berl. Berichte* **47** (1914), 642; *Rend. della R. Accad. dei Lincei* **23** (1914), Ser. Va, 1. sem. fasc. 3. Comp. *Report* April **1904**, 127. — [2]) *Reports* April **1905**, 85; April **1907**, 109; April **1908**, 151; comp. Gildemeister and Hoffmann, *Die ätherischen Öle,* 2nd ed., vol. II, p. 623. — [3]) *Schweiz. Apotheker Ztg.* **52** (1914), 273. — [4]) Comp. the indications on oil of Peru balsam in Gildemeister and Hoffmann, *Die ätherischen Öle,* 2nd ed., vol. II, p. 623.

of these optical results, as one cannot decide whether the balsams designated pure are really unadulterated.

The etheral extract, obtained as above, of *Hardwickia pinnata* balsam deviated —1,3°; that of gurjun balsam, —20,78°; that of Maracaibo copaiba balsam, +0,40°; and that of Para copaiba balsam, —0,83°.

As to the distillation of Peru balsam with steam, K. Dieterich[1]) says that in previous experiments with genuine balsam, he had always obtained only a few drops of a dark yellow oil, congealing to a waxlike mass and smelling like cinnamein, whereas almost all the artificial products yielded a very liquid distillate of a strange odour. In order to decide the question whether, on distilling with steam, genuine Peru balsam would likewise yield more volatile substances, an experiment on a larger scale was made. For this purpose 6 kilos of pure balsam were mixed with the same quantity of boiled-out river sand and most carefully distilled in a still composed of several tiers, with steam of only $1^1/_2$ atmospheres of pressure, so as to avoid, as far as possible, the formation of decomposition products. Out of 1000 litres of aqueous distillate, about 300 grams, *i. e.*, 5 p.c. of the quantity of balsam employed, of an oily substance were obtained, the odour of which resembled that of Peru balsam.

The balsam recovered after the distillation showed in its constants but little difference from the original product; the qualitative tests[2]), however, were partly different. The nitric acid test showed, in opposition to the raw material, not a golden yellow, but a bluish green colour, and with light petroleum quite a lot of a powdery substance was formed, which did not adhere to the glass. The modification of the qualitative reactions is evidently to be explained by the way of heating, and it seems quite possible that, on account of unfavourable results of the nitric acid and light petroleum tests, balsams may sometimes be rejected which are not adulterated but have merely been altered by too much heating when they were obtained from the tree. The author's opinion is that this ought to be taken into consideration when testing Peru balsam. Balsam which does not give correctly the reactions mentioned cannot therefore be marked as adulterated, if other indications are absent, but is nevertheless to be regarded as inferior. It must further be said that, when distilling Peru balsam with steam, certain quantities of its natural components will pass over, which smell just the same as the balsam itself and are thick, oily liquids of yellow colour, but they must not contain any extraneous essential oils and aromatics, the presence of which might be proved by their smell or otherwise.

The volatile oil referred to above, which passed over with the steam, was investigated by A. W. Sortell[3]), and proved to be identical with cinnamein. It forms a yellowish liquid of agreeable smell and of the specific gravity of 1,0869 at 17°; α_{D200} +2,04°; sap. v. 245,7. It chiefly consists of the esters of benzyl alcohol with benzoic and cinnamic acids, the former preponderating considerably; peruviol[4]) is likewise said to be one of the components.

Phenol Methyl Ether, see Anisole.

Vanillin. A so-called vanillin, adulterated in an entirely incredible manner, was recently investigated in our laboratories. It had been sent us from Italy in its original

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[1]) *Berichte der deutsch. pharm. Ges.* **24** (1914), 225. — [2]) Comp. *Report* April **1914**, 107. — [3]) *Berichte der deutsch. pharm. Ges.* **24** (1914), 233. — [4]) *Report* April **1914**, 80.

packing in order to be tested. The wording of the label, which we copy here literally with all its mistakes, ran as follows: —

ÉTABLISSEMENT CHIMIQUE
FONDÉ EN 1880

GIRARD & BLONET
PARIS

VANILLINE CRISTALLISÉE

GARANTIE PURE LE 100/00 KM.

Exstraits Essences Huiles Ethers

DIRECTION: RUE MONTPARNASSE N. 18
FABRIQUE: RUE BOISSIERE N. 62
ADRESSE TELEGRAPHIQUE GIRARD & BLONET

The great inferiority of the stuff was disclosed from the very beginning by the fact that it had no uniform melting point. It began to soften at about 70° and was not completely melted even at 95°, whereas pure vanillin melts distinctly between 80 and 84°. On further examination we found to our surprise that the largest part of the product was salicylic acid, which was characterized by its melting point (about 157°), as well as by transforming it into its methyl ester. It was possible to determine the quantity of salicylic acid with the aid of sodium bicarbonate, with which it reacts, whereas vanillin does not. For this purpose the product was dissolved in ether and the solution shaken with a saturated solution of sodium bicarbonate until the evolution of carbon dioxide had completely ceased. The aqueous solution, in which the salicylic acid was present as sodium salt, was then separated from the ethereal one, acidulated with dilute sulphuric acid and repeatedly treated with ether. The ethereal extracts, which contained all the salicylic acid, were put together and shaken for some time with a solution of sodium bisulphite, in order to get rid of the traces of vanillin, which migth mechanically have passed into the solution. After having removed the sodium bisulphite solution, the ether was distilled off and the residue dried and powdered. From 100 g. of material, 82 g. of salicylic acid were thus obtained, which melted exactly between 156 and 157°. As mentioned already, it was further identified through its methyl ester.

Another sample was at the same time used, with the aid of *p*-bromophenylhydrazine and following the prescriptions of J. Hanuš[1]), to determine the amount of real vanillin contained in the product. It came to about 18 p. c., in accordance with the result of above test.

Taking into consideration that 1 kilo of vanillin cost at the time more than 50 ℳ, and salicylic acid not more than 2.50 ℳ, the profit made on this swindle must have been enormous, even if the price was cut down very low. It is to be hoped that not too many buyers were caught with this "vanillin", which might more appropriately be advertised as a "rheumatism cure with vanilla flavour".

The dissimilar behaviour when melting vanillin from clove oil and vanillin from guayacol, induced M. Lehmann[2]) to study these differences more closely. He points

[1]) *Zeitschr. Untersuch. d. Nahrungs- u. Genussm.* **3** (1900), 531; *Chem. Zentralbl.* **1900**, II, 693. — [2]) *Chem. Ztg.* **38** (1914), 388, 402.

out that, in order to get comparable figures, the temperatures must always be read under the same conditions. Whereas analysts are used to read as melting point the temperature at which a solid substance is completely melted, the German Pharmacopoeia considers as melting point the degree at which the solid body flows together in the melting tube, before being entirely melted. It is therefore necessary to distinguish between the melting point of the German Pharmacopoeia V and clear melting. Much stress is laid on the shrinking, which, as is known, enables one to make reliable conclusions as to the purity of the substance. The purer the preparation, the closer together are the temperatures of shrinking and clear melting, whereas the differences are greatly enhanced already by traces of organic solvents, such as benzene, light petroleum, toluene, &c.

The sulphuric acid test is only of conditional value for estimating vanillin, but combined with other tests it may afford a clue as to the purity of the preparation. Lehmann carried out his investigation as follows: in a cylinder with glass stopper, holding about 30 cc. and which has carefully been rinsed with pure concentrated sulphuric acid, 1 g. of vanillin is vigorously shaken with 10 cc. of pure concentrated sulphuric acid. Pure products dissolve in the acid with orange-yellow colour, whereas inferior ones show a dark yellow to brown colour, according to the kind and quantity of impurities. Lehmann obtained the following results through his investigations:—

	Franz Fritzsche & Co.'s vanillin from clove oil	guayacol-vanillin of different origin
shrinking	79,5°	77 to 79,0°
m. p. as per German Pharmacopoeia V	81,3°	80 „ 81,1°
clear melting	81,9°	81 „ 81,5°
solidification point	81,5 to 82°	81 „ 81,5°
sulphuric acid test	orange-yellow	orange-yellow to brown

He further added, in varying proportions, to pure vanillin the different substances which occur as adulterants and observed the changes in the temperatures of shrinking and melting, taking into consideration the above observations. In the original treatise, the results are perspicuously arranged in the form of tables and are further explained by graphic figures. In addition, it is described how the presence of some well-known adulterants, such as coumarin, heliotropin, benzoic acid, salicylic acid and antifebrin, can be proved.

A publication by C. F. Boehringer & Soehne[1]), who manufacture vanillin from guayacol, is directed against Lehmann's assertion in his treatise referred to that vanillin from clove oil is superior to that from guayacol. At the request of this firm, the Mannheim municipal laboratory examined both kinds of vanillin (Franz Fritzsche & Co.'s vanillin from clove oil and C. F. Boehringer & Soehne's vanillin from guayacol) and found that there was no difference at all in the behaviour when melting, whereas the sulphuric acid test resulted in favour of vanillin from guayacol:—

	eugenol-vanillin (Franz Fritzsche & Co.)	guayacol-vanillin (Boehringer & Soehne)
shrinking	80,7°	80,7°
m.p. as per German Pharmacopoeia V	81,2°	81,2°
clear melting	81,5°	81,5°
solidification point	78,9 and 78,85°	78,9 and 78,95°
id. id. according to Lehmann	80,0 and 80,1°	79,95 and 79,9°
sulphuric acid test	dark orange-yellow	vivid yellow

[1]) *Chem. Ztg.* **39** (1915), 31.

The Mannheim laboratory determined the melting point in an apparatus, prescribed for testing fats by the German Excise Authorities and a picture and description of which are given in the article. Lehmann ascertains the melting point by melting 10 g. of vanillin in a test tube, placed into a water-bath of 90°, allows the melted substance to cool to 76° in another water-bath which has been heated to 75° only, and then adds some crystals. The thermometer rises quickly to the highest temperature, which is considered as the solidification point.

As said before, the investigation at the Mannheim laboratory proved that the melting and solidification points of good clove-oil-vanillin and good guayacol-vanillin are completely identical and that therefore vanillin can be obtained from guayacol just as pure as from eugenol. As regards the preparations tested, Fritzsche's eugenol-vanillin was even inferior to Boehringer's guayacol-vanillin, as far as the look and the sulphuric acid test are concerned, but the manufacture as such of vanillin from clove oil cannot, of course, be held responsible for this. Boehringer & Soehne finally urge how important it is just at present that this much-used aromatic can be manufactured in perfect condition from a coal-tar distillation product, for the German industry, in consequence, becomes independent of foreign countries at a time when the imports of transmarine cloves fail to reach us.

The observation that vanillin is frequently found in soils[1]) and unfavourably influences[2]) the growth of plants induced M. H. Sullivan[3]) to examine wheat germs for their contents of vanillin. He succeeded indeed in finding in the young wheat plants a substance which reacted upon sodium bisulphite and gave the colour reactions, characteristic for vanillin, with ferric chloride (blue), ferrous sulphate and bromine water (green), and with a mixture of hydrochloric acid, sulphuric acid and acetone (violet). Sullivan further determined vanillin by the colorimetric method according to Folin and Denis[4]), thus finding in wheat grains 1 to 6, in wheat digested with 5 p.c. sulphuric acid 5 to 14, in wheat bran 3 and in the various parts of the germs 6 to 18 parts per million of vanillin.

As it is known that more vanillin can be extracted from soils previously treated with sulphuric acid, Sullivan supposes that plants often contain substances, which, on hydrolysis or during the growth of the plants, yield vanillin, and that these bodies are likewise present in the soil as plant secretions.

The author further found vanillin in rotting oakwood, in the pulp and skin of pine-apples and in extracts obtained with hot water from turf grass.

One looks in vain for an exact chemical proof in Sullivan's treatise that he really had to deal with vanillin. To prove the presence of a body in such infinitesimal traces merely by colour reactions, and that not only qualitatively, but also quantitatively, is a rather daring undertaking, the value of which may be disputed.

E. P. Häussler[5]) reports on numerous colour reactions of vanillin. With the aid of phloroglucinol, even 0,000005 g. of vanillin give a distinct, pink colour, and with p-phenylenediamine hydrochloride even 0,0000008 to 0,0000005 g. of vanillin may still be detected by a feeble, yellow coloration during evaporation. Altogether, Häussler describes 27 different colour reactions of vanillin. Teresantalic acid may likewise be

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[1]) E. C. Shorey, *J. Agr. Res.* **1** (1914), 357. — [2]) Schreiner and Reed, *Bull.* 47, *Bur. of Soils, U. S. Dept. Agric.* (1907); Schreiner and Skinner, *Bull.* 77, *Bur. of Soils, U. S. Dept. Agric.* (1911). — [3]) *Journ. Ind. Eng. Chemistry* **6** (1914), 919. — [4]) *Journ. Biol. Chemistry* **12** (1912), 233. — [5]) *Zeitschr. f. anal. Chem.* **53** (1914), 363, 691; *Chem. Zentralbl.* **1914**, II. 86; **1915**, I. 221.

used as an indicator of vanillin; on evaporating with vanillin and sulphuric acid, it gives a red coloration, which gradually passes into violet, and evolves a camphor-like odour.

Nothing is said in the treatise as to whether similar colour reactions are to be noticed with bodies allied to vanillin. Generally speaking, such reactions fail as soon as the substances in question are not pure but mixed with other bodies that frequently influence the reaction.

Häussler further carried out reactions of vanillin with albumen (from eggs and blood), fibrin, casein, Witte's peptone, rennet and pure gelatine; he likewise determined what colour reaction urea gives with vanillin. It resulted that by means of the vanillin reactions albuminous substances can be detected with certainty, on the one hand among their resolution products, on the other, most likely also among enzymes. Proteins give with vanillin and hydrochloric or sulphuric acid a reddish blue-violet coloration, which proteids do not. The decomposition products of protein and allied compounds show the characteristic, sulphur-yellow colour, owing to their amide and imide groups, whereas in combinations obtained with the aid of alkalis or through decay, such as indole and scatole, a red colour results. Urea behaves in a similar way.

In order to find out the constitution of the coloured compounds, vanillin was condensed with sulphanilic acid, when potassium 1-hydroxy-2-methoxy-4-benzylidene-1-aniline-4-sulphonate, a crystalline powder of orange-red colour, is formed.

Notes on Scientific Research in the Domain of the Terpenes and Essential Oils.

General.

Trial cultivation in Usumbwa.

In a report by H. L. Hammerstein[1]) on part of the trial cultivations hitherto carried out in the Tabora district, Usumbwa territory, German East Africa, we likewise find something interesting for our special domain, *e. g.* that betel pepper (*Piper Betle*, L.) prospers fairly well in soil to which lime has been added. It climbs on *Ficus* species, but is very sensitive as regards intense insolation.

The *Juniperus procera*[2]) trees (Usambara cedar), now 2 years old, are of vigorous growth and have attained a height of 1 m. The prolonged drought in that region has not had any influence on their development. All *Eucalyptus* species have much to suffer from termites. Two year old specimens of *Eucalyptus robusta* and *rudis* have now attained a height of up to 4 m., and the diameter of the trunks comes to about 10 cm. Citronella grass prospers; the propagation is effected by suckers. *Andropogon citratus* is indicated as mother plant, so that there seems to be a confusion with lemongrass.

Grafted young Italian lemon trees, received from Amani in December, blossomed after barely 3 years, and some formed fruit. Plants derived from seeds are still far behindhand. Limetta trees grow rather slowly. Genuine, grafted Italian orange trees flourish best. Seedlings grow very slowly at first; the seeds often take 5 to 6 months to germinate. Mandarine trees get on slowly and are highly sensitive as regards burning sunshine. The nutmeg trees died. Ginger grows slowly; cardamoms flourish better. Caraway and anise do not form seed; coriander grows well. Many other plants of the spice and kitchen herb line flourish well or in any case satisfactorily, *f. i.* balm (melissa), chervil, fennel, dill, marjoram, thyme, estragon, satureja, and parsley.

Cultivation of medicinal plants.

From E. Senft's[3]) communications on trial cultivation of medicinal plants at Korneuburg in 1913, we gather some data of general interest concerning aromatic plants. Fromthe group of vegetal parasites, *Puccinia Menthae* ought to be mentioned. Japanese peppermint suffered most from it. Leaf-lice *(Aphis Angelicae* and *Ligustici)* caused damage in angelica and lovage fields.

Larvae of beetles *(Agriotes)* and multipeds *(Blanjulus)* damaged angelica roots. In autumn 1912, angelica seed was sown on a small piece of land; during the spring following the plants developed fairly well, but later on large gaps appeared, owing to the damage done by multipeds. Many rootlets were much eaten; the main roots,

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[1]) *Der Pflanzer* **10** (1914), 224. — [2]) The wood of *Juniperus procera* is used in the manufacture of lead-pencils. Comp. *Report* October **1911**, 106. — [3]) *Zeitschr. f. d. landwirtsch. Versuchsw. in Österreich*, 1914, Part 3/4. *Mitteilungen des Komitees zur staatlichen Förderung der Kultur von Arzneipflanzen in Österreich* Nr. 17. From a reprint kindly sent us.

sometimes pierced. Further reports are made on the plantations of Roman chamomiles, wormwood, estragon, spoonwort, lavender, lovage, balm (melissa), peppermint, *Mentha canadensis* (Japanese peppermint), spearmint, *Mentha viridis*, *Mentha* from Admont (Styria), from Bohemia, from Moravia, winter marjoram, garden rue, parsley, sage, *Salvia Sclarea*, tansy, thyme, hyssop and valerian.

In addition to the simple Roman chamomiles *(Anthemis nobilis)*, there was another variety of cultivation, *Anthemis nobilis* var. *β-floscula*, Pers. (*Anthemis aurea*, DC.), which distinguishes itself by having lost the marginal flowerets completely. This variety is said to have a specially strong aromatic odour (see page 39 of this *Report*).

Manuring experiments gave satisfactory results with wormwood. The yield amounted to 98,6 kilos of fresh and 24,2 kilos of dried herb per 100 square m. for a manured piece of land, and 63,1 kilos and 16,15 kilos, respectively, for unmanured soil. Wormwood-growing in Austria pays only where ground and labour are cheap. Wormwood does not require any special care, aside from keeping the field free from weeds. In consequence, waste grounds, slopes, &c. are best adapted for it, where it can spread by itself. Wormwood, which has again run wild, is sometimes preferred to the cultivated plant.

From a surface of only 8 square m. not less than 47,9 kilos of fresh estragon herb were collected.

Spoonwort was sown on April 30th. On October 8th the plants were put on a piece of land freshly prepared. They stood the winter very well and sent out flower stalks already at the end of February; at the beginning of May the field was in full bloom. Cutting caused not only fresh leaves to form, but likewise fresh flower stalks.

Senft thinks a successful cultivation of lavender impossible at Korneuburg, as lavender requires protection against wind.

It is worth mentioning that lovage was the only plant which did not suffer from canker-worms.

On unmanured soil, 8,6 kilos of spearmint were obtained per 100 square m., whereas a manured piece of land yielded 15,87 kilos. Spearmint leaves are crisped and rather short in proportion. These crisped leaves extend remarkably, however, when the plant forms flowers; the crisped border then disappears and the aspect of the plant changes altogether.

The peppermint plants got through the winter rather badly. They remained low and looked sickly; some turned reddish at first, then brown, and died. The cause of this disease has not been found so far.

Mentha viridis seems to be very resistant against *Puccinia;* the disease was neither noticed at Korneuburg, nor elsewhere. A plantation of a peppermint variety, cultivated in the marsh farm at Admont (Styria), was almost entirely destroyed by parasites.

In order to obtain parsley roots, it seems to be advisable to cut down the flower stalks, so that the roots can get stronger.

Hyssop and garden rue yielded less on a manured piece of land than on unmanured ground.

Sage frequently suffered from the winds generally prevailing at Korneuburg. Moreover, sage must never be left over 3 years in the same place, as the yield generally diminishes considerably already in the 4th year. Like rue, sage is unfavourably influenced by stable manure.

A plantation of thyme had developed very well and not suffered at all from the drought early in 1913.

A plantation of valerian was almost entirely destroyed by canker-worms.

As far back as 1904, B. Pater[1]) tried to cultivate medicinal plants at Klausenburg. He now reports on spearmint and peppermint. Spearmint was cut first at the end of June, then again at the end of September, and a third time between October 17th and 22nd. In order to find out what effect the third cut might have, he left half the field untouched; it turned out the next year that the third cut had not had any influence on the plants getting through the winter. He recommends as the best remedy against *Puccinia Menthae* to cut the plants earlier and not to wait until the flowers appear. It is true, one generally imagines that the plant is richest in oil when flowering, but it must be taken into consideration that the leaves attacked by *Puccinia* are without any value. *Puccinia* seems to spread from the soil, for the bottom leaves show the disease first, and then it spreads upwards.

Pater further describes the properties of Hungarian spearmint oil, on which we have reported before now[2]). Experiments of perfuming soap with spearmint oil gave very favourable results. An antiseptic soap of pleasant odour was thus obtained, which made the skin soft and smooth.

Pater reports fully on his experiments with peppermint. He cultivated plants which came from Rev. Josef Agnelli's plantation at Csári and which he calls *Mentha piperita* var. *Agnelliana*. The herb was dried naturally as well a artificially, this in a heatable hop-oast. The naturally-dried peppermint contained 0,7024 p. c., that dried artificially, 0,8844 p. c. of oil. Peppermint planted in spring 1908 was already in 1912 very weak and degenerated, so that it could hardly be used. The soil was poor and exhausted from the outset, which accounts perhaps for the failure of the experiment.

The properties of Hungarian peppermint oil[3]), as well as of *Oleum Menthae aquaticae Hung.*[4]), were described by us already three years ago.

Experiments with Mitcham and Japanese peppermint are also being made (see page 34). About 80000 slips of Mitcham peppermint are required for 1 hectare of land.

In 1904, Pater planted pieces of rhizomes, taken from calamus plants from a pond close by, on a bed which could easily be watered. In October 1906 the calamus was well developed. The bed had, it is true, frequently been weeded, hoed and manured. The result was satisfactory.

The cultivation of violets in southern France.

In an article published by a French horticultural journal[5]), we find an exact description of the cultivation of violets in southern France, as well as statistics of the export of violets from Hyères. The cultivation was begun there about 30 years ago; it has developed to such an extent, that in winter more than 500 parcels of 3 kilos each are sent off daily. There are 500 to 600 women employed in the gathering. Of late years, Vence, a village in the Maritime Alps (*arrondissement* Grasse), seriously competes with Hyères. For half a century, flowers for the perfumery industry had been grown at Vence, but on account of the low prices offered by the manufacturers, a start was made to cultivate violets for the export of the flowers, with remarkable success. The varieties mostly planted are "Victoria" and "Princesse-de-Galles".

At Hyères, the violets are still frequently grown on open fields, but of late the growers have begun to cover the plantations slightly against frost, which causes the flowers to appear sooner.

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[1]) *Die Heilpflanzenversuchsanstalt der landwirtschaftlichen Akademie in Kolozsvar*, Part 1; Kolozsvar 1914. — [2]) Comp. *Report* April **1912**, 118. — [3]) Comp. *Report* April **1911**, 91. — [4]) Comp. *Report* April **1912**, 132. — [5]) *Bull. Soc. Hort. Nice* **17** (1913), 373; *Bull. Sciences pharmacol.* **21** (1914), 234.

Directions how to collect and preserve plants in foreign countries.

For those desiring to send home plants from distant regions or to collect plants in foreign countries for scientific purposes, an article in the well-known "Kew Garden Bulletin of Miscellaneous Information" gives useful, adequate directions[1]). If it is a question of collecting new material for gardeners, seeds are preferable to living plants or cuttings. Some plants, however, such as orchids, many tuberous plants *(Aroideae)* and some *Zingiberaceae* cannot, or only with difficulty, be raised from seeds. The seeds must be ripe and dry and are best forwarded in small canvas bags. Hermetically sealed tins and bottles are not to be recommended, as seeds keep better if change of air is possible. Bulbs and rhizomes should only be collected after the period of vegetation is over and must be kept dry for some days, until the leaves have faded. They are best forwarded in wooden boxes and packed in wood shavings, paper, or some other dry, light material. Straw and hay cannot be recommended, as they rot easily. If the rhizomes are weakly and thin, they are best packed in a light, slightly moistened material, such as cocoa-nut fibres, peaty soil, sawdust or wood shavings. Rhizomes and seeds of aquatic plants and ferns are best sent in damp moss. Cuttings, *e. g.* of *Pelargonium* species, should be packed in oiled silk and then placed in tins or wooden boxes. Many plants, such as pelargoniums, which are very resistant against drought, may be put into wooden boxes, the roots being tightly packed in moss, wood shavings, banana leaves, &c. Seeds for museums may be sent dry without any special precautions. If damage through insects is to be feared, carbon disulphide must be poured over the seeds, or naphthalene, added before packing in tin boxes. Cones of conifers, which open when dry, must be tied up with string, so that they cannot lose seeds on the way. Soft fruits are placed in bottles with alcohol, rum, salt water or a 5 p. c. formaldehyde solution. Fruits and succulent plants may likewise be kept in alcohol or formaldehyde for several hours and then wrapped up in cotton wool, impregnated with said preservatives.

Another part of the article refers to the collection of material for herbariums. As a general rule, only complete material ought to be taken, *i. e.* plants with flowers and fruits. When drying, the universally known rule is to be followed to press little at the beginning and a little harder later on, but to avoid too much pressing altogether. It is of great importance sometimes for later investigation to have some flowers preserved in alcohol, formaldehyde, or salt water.

A method recommended by Schweinfurth is complicated, it is true, but affords excellent results. The plants are placed between paper, as usual, and then put in layers into tin boxes, exactly described in the original, after alcohol has been poured over the whole. The tin boxes are then soldered, and the plants, which thus keep for a fairly long time, may be dried later on, when there is a favourable opportunity. This method has a very great advantage during rainy periods. It is self-evident that the material must be carefully labelled.

The world's production of essential oils.

J. C. Umney[2]) discusses the world's production of essential oils in a very exhaustive article. He indicates, for almost every country, which plants are grown and collected for the manufacture of volatile oils or might come into consideration for the purpose. It seems that he bases his inferences on indications regarding the smell of the various plants, as are found here and there in books, so that many of his suggestions will

[1]) *Kew. Bull.* **1914**, 97. — [2]) *Perfum. Record* **5** (1914), 164.

presumably have no practical value. The article further contains statistics the production and export of the most important essential oils.

Occurrence of fragrant plants in Hawaii.

In the same periodical, we find an article[1]) on the occurrence in Hawaii of a plant smelling like violets and which is called there either *"Pakalang"* or "Chinese violet". Holmes presumes that this plant is *Pergularia fragrantissima,* an *Asclepiadacea*[2]). The aromatic principle of the flowers can be extracted by way of "enfleurage". In addition, a plant referred to as *"Mulang"* is cultivated, which most likely is identical with the champaca shrub *(Michelia Champaca). Acacia Farnesiana* likewise occurs in Hawaii under the name of *"Klu"*. E. V. Wilcox[3]) points out the possibility of using this plant for the manufacture of scents.

Bibliography.

The valuation of copaiba balsams is rendered rather difficult by the fact that almost nothing is known as to the properties and composition of genuine, unadulterated balsams. The products reaching Europe have, perhaps, been more or less sophisticated in the country of origin. An improvement of the conditions is to be expected only if chemists, perhaps together with botanists, personally collect samples of South American balsams on the spot and determine the relative physical and chemical properties. Once it is known within what limits they oscillate in normal products, it will be possible to put the commerce of copaiba balsam on a sounder footing, which would surely contribute to secure a more frequent and successful use of the balsam and its oil than hitherto. In order to make a start in this direction, E. Deussen wrote a treatise[4]) under the title of *Copaivabalsame und ihre Verfälschungen nebst den Anforderungen der wichtigsten Arzneibücher an den offizinellen Copaivabalsam* (Balsams of Copaiba and their adulterations, along with the requirements of the most important pharmacopoeias concerning officinal balsam), which gives a complete summary of the copaiba balsam literature. He discusses first the South American copaiba balsams, then illurin balsam (so-called African Balsam), gurjun balsam, the wood oils from the Philippines, cedarwood oil, segura balsam, balsam of *Hardwickia pinnata* and lagam balsam. In the second part of his publication he deals with the principal working and testing methods and, in an appendix, mentions the requirements formulated by the principal pharmacopoeias for officinal copaiba balsam.

K. Hassack gave a lecture on the production of natural and artificial aromatics, which he published later on in the form of a booklet[5]).

W. Müller[6]) reports on the progress in the domain of the chemistry of the terpenes and aromatics, made from May 1913 to June 1914. A. Reclaire[7]) published reports of the progress in the domain of the terpene and essential oil chemistry in 1912 and 1913 and of the progress in the domain of the essential oils and aromatics (July 1913 to August 1914).

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[1]) *Perfum. Record* **5** (1914), 130. — [2]) The *Index Kewensis* does not mention this species, but *P. odoratissima,* Sm., probably indigenous in Further India and which is largely cultivated in East Asia and East India on account of its sweet smelling flowers. — [3]) *Americ. Perfumer* **9** (1914), 75. — [4]) Leipzig, 1914; published by *Winter's Verlagsbuchhandlung.* — [5]) Graz, 1914. Published by the *K. k. Lehrmittelbureaus für kommerzielle Lehranstalten.* From a copy kindly sent us. — [6]) *Fortschritte der Chemie* **10** (1914), 95, 183. — [7]) *Chem. Ztg.* **38** (1914), 729, 770, 783, 874, 939. — *Zeitschr. f. angew. Chem.* **27** (1914), I, 572, 577.

On page 42 of this *Report*, a booklet on *Shô-Gyū* and *Yu-Ju* oils, published by K. Nagai with many illustrations and maps, has been discussed.

O. Simon[1]), in an article on the principles of obtaining essential oils by distillation, and on steam distillation generally, gives a short description of the distilling apparatus, the preparation of the raw materials and the various ways of distilling, ending up with some remarks on the theory of distillation.

O. Volz[2]), in an article well worth reading, describes the development of the industry of scents and aromatics in a very concise form. After a short historical introduction, he deals with the production of essential oils from plants by steam distillation, the manufacture of synthetic aromatics, of scents and, finally, of toilet soaps.

Analytical Notes.

Change of density and of index of refraction of essential oils according to the temperature.

As ascertained by experiments, carried out in our laboratories some years back[3]), the density of a number of essential oils changes in comparison with water of 15° by about 0,00075 for every degree centigrade. On account of observations, made with about 45 different essential oils, K. Irk[4]) indicates the modifications of the specific gravity for 1° centigrade as follows: between $d^{15°}_{4°}$ and $d^{20°}_{4°}$ 0,0008; between $d^{15°}_{15°}$ and $d^{20°}_{15°}$ 0,0007; between $d^{15°}_{15°}$ and $d^{20°}_{20°}$ 0,0006; in round figures.

For numerous essential oils, K. Irk[5]) likewise determined the change which the index of refraction underwent according to temperature. It amounts for 1° centigrade: between 15 and 20° to 0,00043 in the mean; between 10 and 15° to 0,00043; between 20 and 30° to 0,00045 and between 10 and 30° to 0,00044; *i.e.* on an average 0,00044. His observations, made with 50 different oils, are given in the form of tables.

We observed at the time a change of 0,00035 on an average for every degree of temperature[6]).

Estimation of esters in volatile oils.

When estimating esters in volatile oils under apparently equal conditions, results are obtained sometimes which do not tally. According to A. Béhal's[7]) indications, the differences come up to 3 p. c. The same observations are made when one tries to determine the composition of a formate or acetate. The author sees the cause of these differences in that during the saponification esters are formed intermediately, which boil very low perhaps and may thus escape through the condenser. As he ascertained experimentally, the esters are decomposed by potash lye in the presence of an alcohol, when a certain quantity of the ester of the alcohol of the lowest molecular weight is formed and the alcohol of the highest molecular weight split off. When heating for instance cocaine, or the benzoates of phenol, *p*-chlorophenol, *m*-cresol, creosol, eugenol, &c. with alcoholic half normal potash lye, a certain quantity of ethyl

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[1]) *Seifenfabrikant* **34** (1914), 1299, 1318. — [2]) *Der Siegeslauf der Technik.* Edited by M. Geitel. II. ed., p. 353. From a reprint kindly sent us. — [3]) *Report* October **1905**, 87. — [4]) *Pharm. Zentralh.* **55** (1914), 831. — [5]) *Ibidem* 789. — [6]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 561. — [7]) *Bull. Soc. chim.* IV. **15** (1914), 565.

benzoate is obtained. The reaction can be beautifully demonstrated by heating the almost inodorous benzyl benzoate for a few minutes with alcoholic potash lye, when the characteristic odour of ethyl benzoate will become noticeable; odourless benzyl salicylate yields with methyl alcoholic potash the distinctly smelling methyl salicylate (wintergreen oil).

In an analogous way ethyl formate and ethyl acetate are formed, when the formates and acetates of essential oils are determined. The quantities produced are largest if the amount of alkali added is insufficient for the saponification. In the presence of a quantity of alkali sufficient for complete saponification, when but very small amounts of volatile esters are formed, and by using a water reflux condenser, losses owing to volatilization are not to be feared. As safest protection against losses, Béhal recommends saponification in a closed vessel at the temperature of the water-bath.

According to our experience, it is sufficient to use a condensing tube about 1,5 m. long, in order to avoid losses of volatile esters, so that the intermediate reaction is without influence on the accuracy of the usual ester determination.

Jean Nivière[1]) turns against Béhal's suggestion to saponify the esters in a closed vessel. He first proves by comparative experiments that the classical method of saponification[2]) affords exactly tallying results, if on the one hand a condensing tube 1 m. long, and on the other hand a water condenser 50 cm. long are used. On the other hand saponification in a closed vessel cannot be recommended, as the ester numbers of lavender and bergamot oils thus obtained are 3,8 or 1,6, respectively, higher than those found under ordinary pressure.

As formerly stated also by us[3]), a small absorption of alkali was noticed in saponifying linalool which had been purified by fractionated distillation. We then were of opinion that only during saponification in a closed vessel part of the linalool was decomposed owing to the heating under pressure and that the saponification number found in this way was but illusory. According to Nivière's experiment, it would seem, however, as if linalool purified by distillation still contained small amounts of esters, and that pure linalool is not attacked, even when heated under pressure; for, after one sample had shown the same saponification value in either way of saponification, the same linalool, upon rectification with steam in the presence of a little alkali, showed no further absorption of alkali, neither when heated in an open nor in a closed vessel. Furthermore, the same saponification value was found for pure linalyl acetate in either way of heating. From his experiments, Nivière draws the conclusion that the increase of the ester value when heating under pressure is not due to the action of alkali on linalool, but probably to the influence of other bodies, such as aldehydes. He finds this supposition confirmed in that, after adding 2 p.c. of oenanthol to linalyl acetate, the ester value under pressure was 2,0 higher than that found in the usual way of saponification.

Determination of the "hydrogen number" of volatile oils.

In order to estimate certain volatile oils, A. R. Albright[4]) determines their hydrogen number[5]) in a complicated shaking apparatus, which he describes minutely and of which he gives some illustrations. By hydrogen number he understands the number of cc. of hydrogen which, at 0° and 760 mm. pressure, are taken up by 1 g. of oil during the

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[1]) *Bull. Soc. chim.* IV. **15** (1914), 677. — [2]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 572. — [3]) *Report* October **1895**, 25. — [4]) *Journ. Americ. Chem. Soc.* **36** (1914), 2188. — [5]) Comp. S. Fokin, *Chem. Zentralbl.* **1908**, II. 2039.

period of quickest absorption. As soon as the chief constituent of an essential oil, for instance eugenol, has been reduced, the hydrogenation generally slackens down at once, and this moment can easily be found by entering on a curve, every 15 seconds during the process of reduction, the time and the quantity of hydrogen absorbed. As soon as the main reaction is over, the curve shows a sharp bend, and the hydrogen number may then be read off direct from the curve, taking into consideration the temperature and the pressure. The apparatus consists of a vessel which serves as a receiver for the catalyst (colloidal palladium), the diluting liquid (50 p.c. alcohol) and the substance to be tested. By means of an india-rubber tube, the vessel is joined to a U-burette, which contains the hydrogen. After the air in the apparatus has been replaced by hydrogen, 0,02 g. of dry colloidal palladium is put into the vessel and 50 cc. of 50 p.c. alcohol added. The vessel is then shaken until no more hydrogen is absorbed. Thereafter the substance to be estimated is added, the shaking repeated and the result read as soon as the main reaction is over. In this way 4,63 g. of purified technical safrole, in the presence of 0,1 g. of colloidal palladium and 40 cc. of 50 p.c. alcohol, absorbed 720 cc. of hydrogen at 22° and 758 mm. pressure, which corresponds to 632 cc. at 0° and 760 mm. pressure. Theoretically 641 cc. are required. The dihydrosafrole thus obtained boiled between 234,3 and 234,5°. In the same manner were reduced: limonene, a kind of artificial sassafras oil (a mixture of 4 parts of safrole and 1 part of limonene), genuine sassafras oil, pure anethole, an "artificial aniseed oil" (a mixture of 8 g. of anethole and 2 g. of limonene), current clove oil and oil of pimento. Albright is trying to simplify his apparatus, so that his method may be put to practical use.

The results of the experiments are given in the following table:—

substance	hydrogen number	% active substance	theoretically
safrole	135,6	98,3	100,0
artificial sassafras oil	111,9	81,1	80,0
genuine sassafras oil	103,1	74,8	—
	102,0	74,0	—
anethole	150,5	99,6	100,0
artificial aniseed oil	125,1	82,4	80,0
current aniseed oil	125,8	82,9	—
	127,3	83,9	—
current fennel oil	101,3	66,8	—
	102,7	67,7	—
eugenol	134,4	98,3	100,0
artificial clove oil	113,2	82,8	80,0
	113,3	82,8	80,0
current clove oil	114,6	83,8	—
	114,0	83,3	—
current oil of pimento	97,8	71,5	—

Identification of essential oils in victuals.

In order to identify essential oils in victuals, patent medicines and liqueurs, J. Cerdeiras[1]) determines the behaviour of the oil towards vanillin and hydrochloric acid. This reagent is prepared by dissolving 0,5 g. vanillin in a little alcohol, to which as much hydrochloric acid ($d_{15°}$ 1,10) is added as is necessary to bring the

[1]) *Pharm. Zentralh.* **55** (1914), 339.

total to 100 g. To 5 cc. of this reagent he adds 1 drop of the oil to be tested, shakes thoroughly, and allows the mixture to stand for a quarter of an hour at ordinary temperature, but protected against daylight; he then heats it for 5 minutes on a boiling water-bath and finally shakes it with chloroform after cooling. The colorations during the three treatments are noted and compared with the indications of the tables mentioned below, or with samples of oils already known. When shaking with chloroform, the colouring matter passes into this, and different shades may then more easily be recognized. Cerdeiras tested in this way 42 different essential oils. He gives the results in the form of tables, in which are indicated: the colouring of every oil shown after a quarter of an hour, *id.* after 5 minutes' heating on a water-bath, and the colour of the chloroform after shaking out.

Quantitative estimation of camphor in camphorated alcohol.

In order to determine the contents of camphor in camphorated alcohol, W. B. D. Penniman and W. W. Randall[1]) pour an exactly measured quantity of this preparation into a flask with graduated neck (Babcock's milk bottle), adding an aqueous solution of calcium chloride (d 1,37) until the liquid comes up to the neck. They then add exactly 1 cc. of light petroleum (b. p. 40 to 60°) and fill up with calcium chloride solution until the top graduation mark is reached. After the flask has been shaken thoroughly, it is put into a centrifugal machine for about 5 minutes. Should the calcium chloride solution still not be clear after this, the process is repeated. The increase in volume of the ether zone corresponds to the amount of camphor contained in the camphorated alcohol. In the same manner the contents of essential oils in essences, such as peppermint or lemon essences, may be determined.

Quantitative estimation of aldehydes.

M. Tiffeneau[2]) recommends the use of melubrin (sodium phenyldimethylpyrazolone amidomethanalsulphonate) for the quantitative estimation of aldehydes. He describes the determination of benzaldehyde in cherry-laurel water and of heliotropin (m. p. ?) in commercial preparations. In this latter case he proceeds as follows: 0,20 g. of heliotropin are dissolved in 1 cc. of 96 p. c. alcohol, and a solution of 1,5 g. of melubrin in 4 cc. of water is then added. The next day, the deposit is collected on a weighed filter, dried and weighed. Tiffeneau thus found, as an average for two tests, 0,42 g. of piperonylidenaminopyrine, which indicates that the heliotropin used was 94,3 p.c.

It still remains to be decided whether this result is due to lack of purity in the preparation or to defects of the method of testing.

As to colour reactions of vanillin see page 61 of this *Report.*

Determination of eucalyptol according to Dodge's oxidation method.

In our *Report* of April **1913** (page 62) we discussed a method proposed by F. D. Dodge for determining eucalyptol in eucalyptus and cajuput oils. It is based upon the fact that cineol is comparatively stable under the action of potassium permanganate, and is carried out as follows: the volatile oil in question is shaken with a 5 to 6 p.c. solution of potassium permanganate, which is gradually added under cooling with ice-water, until there is an excess of it. The quantity of the eucalyptol

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[1]) *Journ. Ind. Eng. Chemistry* **6** (1914), 926. — [2]) *Bull. Sciences pharmacol.* **21** (1914), 71.

thus remaining is determined, and its constants are examined in order to find out whether it is pure.

As stated in our above *Report,* we obtained quite unsatisfactory results when testing made-up mixtures according to this method. The mixtures having been adapted in their composition to eucalyptus and cajuput oils, the unfavourable results were directly applicable to the oils themselves. C. T. Bennett[1]) has come to a similar opinion of this method.

Dodge[2]) has now published an answer to these criticisms, in which he advocates once more the suitability of his method. He reproaches us as well as Bennett with not having sufficiently observed his indications, reducing on the one hand the quantity of oil to half and, on the other, not examining the cineol separated off as to its purity. Such an examination, however, was absolutely necessary in order to establish the completeness of the oxidation and to avoid too high results. A loss of cineol was possible by oxidation of part of it, but the reaction could be so conducted that this question was of no practical importance. Dodge himself thinks his method inadequate for oils of a cineol content of less than 50 p. c., but does not consider this of any consequence, as such oils do not generally come into consideration for pharmaceutical purposes. Endeavours to simplify the method in one direction or the other have failed, but it was found that, except at the beginning of the oxidation, strong cooling is required. Only when the reaction slackens down, it may be continued at ordinary temperature.

The reply as rendered above cannot alter in the slightest degree our opinion as to the unsuitableness of Dodge's test. If one followed his suggestion to experiment with each oil until in every isolated case the correct conditions for testing have been found out, it would mean such a loss of time and material as no one can ordinarily afford.

Physical Notes.

See page 81 as to synthesis under the influence of light.

Concerning modification of density and of index of refraction of essential oils according to the temperature, see page 68 of this *Report.*

Absorption curve of some ketones.

In a treatise by G. G. Henderson, J. A. R. Henderson and J. M. Heilbron[3]) on the selective absorption of ketones, we find a description of the curves of absorption of fenchone, camphor, menthone, *cyclo*hexanone, *m*-, *o*-, and *p*-methyl*cyclo*hexanone, carvone, methylheptenone, in addition to other numerous ketones of no interest for our special domain. Some of the ketones used in these experiments were purified by being converted into their semicarbazones, others by means of the disulphite compounds or by repeated distillation.

Occurrence of natural camphor in different forms.

It has been found that natural camphor possesses the quality of crystallizing in different forms. F. Wallerant[4]) observed that, at ordinary temperature, camphor deposits

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[1]) *Perfum. Record* **3** (1912), 295; *Report* April **1913**, 63. — [2]) *Journ. Ind. Eng. Chemistry* **6** (1914), 863. — [3]) *Berl. Berichte* **47** (1914), 876. — [4]) *Compt. rend.* **158** (1914), 597.

from alcoholic solutions in rhombohedric, pseudocubic crystals (1:1,2636), which, under pressure, form twins towards the three surfaces of the rhombohedron. On the other hand at least four different modifications are obtained from the melted camphor on crystallizing. When melted between two glass plates, cubic crystals form, which at 97° become rhombohedric and exhibit but slight birefraktion. They form twin crystals like those obtained from alcoholic solutions. However, they are not identical with these, for small crystals appear at their borders which finally occupy the entire mother crystal and do not distinguish themselves in any way from it. The transformation is irreversible and takes place very slowly, but somewhat more quickly at increasing temperature. The rhombohedric crystals change at — 28° into likewise rhombohedric ones, but which are highly birefractive.

Wallerant also experimented with artificial camphor. Racemic camphor becomes cubic at 94°, probably owing to impurities, but even below — 27° it cannot be transformed into the highly birefractive crystals.

Specific rotation of camphor in olive oil.

The specific rotation of camphor in olive oil has been determined by H. Malosse[1]). For values of q between 75 and 95, it is as follows:—

$$[\alpha]_{D18^\circ} = -57{,}9 - 0{,}53399\,c + 0{,}02834\,c^2 - 0{,}0005023\,c^3,$$
$$[\alpha]_{D18^\circ} = -57{,}9 - 0{,}4894\,p + 0{,}023805\,p^2 - 0{,}0003867\,p^3,$$
$$[\alpha]_{D18^\circ} = -139{,}69 + 7{,}3294\,q - 0{,}092205\,q^2 - 0{,}0003867\,q^3,$$

when c represents the number of grams of camphor in 100 cc. of solution,
p " " " " " " " " 100 grams " " , and
q " " " " " " olive oil " 100 " " " .

Malosse constructed a curve for the specific rotation of camphor in olive oil, from which it is to be seen that the specific rotation increases with the dilution.

We would mention that many years ago already investigations were carried out as to the power of rotation which camphor shows in different solvents. Vogel, *e. g.*[2]), found that the specific rotation of camphor in *iso*valeric and capronic acids decreases at first in a very small degree, reaches a minimum and rises very considerably only if the solution is very strongly diluted.

Rotation of camphor floating on water.

The well-known phenomenon that small pieces of camphor vividly rotate when thrown on water, is explained by Marcelin[3]) through the solubility, though small, of camphor in water. The movement ceases as soon as the vessel, in which the camphor floats on water, is covered, if the solution is saturated, but starts again after removal of the cover. In consequence, the movement of the camphor would have to be ascribed almost exclusively to its being dissolved and only in a very small degree to its sublimation. The thickness of the filmy camphor layer on the water equals the diameter of a camphor molecule.

As to the behaviour of santenone when exposed to the light, see page 95.

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[1]) *Bull. Soc. chim.* IV. **15** (1914), 358. — [2]) H. Landolt, *Das optische Drehungsvermögen.* 2nd ed. Braunschweig 1898, p. 176. See also *Reports* October **1911**, 123; October **1912**, 159. — [3]) *Annal. de Phys.* IX. **1** (1914), 1; *Chem. Zentralbl.* **1914**, I. 1048.

The absorption spectrum of buchu camphor.

On investigating the absorption spectrum of buchu-camphor in ultraviolet light, M. Mayer[1]) found that it shows an absorption band, the maximum of which coincides with an oscillation number of 3750 and a longitude of the waves of 268. It shows, besides, the absorption in the extreme ultraviolet which is common in many colourless organic substances.

Pharmaco-physiological Notes.

Remedies against vermin.

In the *Institut für Schiffs- und Tropenkrankheiten* at Hamburg, S. v. Prowazek[2]) made some experiments as to the extermination of fully-grown lice. He found that the matured lice are more sensitive than the younger, more lively ones. Leaving aside the steam disinfection, as well as the light petroleum method, the remedies, which shall principally benefit the soldiers, who, especially in the East, are fighting under very difficult conditions, must fulfil the following requirements: 1. their application must be easy and possible even under the most primitive conditions; 2. they must not soil the skin, the clothing or the linen; 3. they must not be too volatile or inflammable; 4. they must be easily obtainable in times of war. All these requirements are fulfilled by the essential oils, among which eucalyptus, clove, fennel and above all aniseed oil rank first. According to the experiments carried out so far, the lice ought to be killed with embrocations of 30 to 40 parts of aniseed or fennel oil in 70 or 60 parts, respectively, of 96 p.c. alcohol.

Soldiers at the front are said to have found menthol very useful too as a means of protection against insects[3]). It is reported that it is sufficient to rub the boots and the socks with a menthol stick, in order to prevent the vermin from creeping up on the body. Pencilling the clothes with the stick will drive away such vermin as may be already on the body. Diluted carbolic acid is likewise said to be of use.

According to Galewsky's[4]) experiences in the prisoners' camp at Königsbrück, oil of bergamot acts most promptly of all, then aniseed and fennel oils. As fennel oil is scarcely to be had at present, it is advisable to use the cheaper anethole. The effect generally lasts only for a few days (the oils are applied in 10 to 15 p.c. alcoholic solutions). The following mixture seemed to be most effective: 10 g. oil of bergamot, 30 g. tincture of calamus and sufficient alcohol to make up 100 g.

On page 55 we have reported on the excellent effect of anisole (phenol methyl ether) against vermin.

Strength of odour of some essential oils.

J. C. Umney[5]) examined 42 different essential oils as to the constancy of their odour on evaporating when exposed to the air. He put a certain quantity on filter paper, exposed this to the air at room temperature and compared the smell after 1, 2, 3, 4, 5, 7 and 14 days with what it had originally been. The tables compiled by Umney show that the odour of juniper and wintergreen oils disappeared already after one day, whereas patchouly oil has the most lasting odour. Eight of the most important oils range as follows: patchouly, sandalwood, cinnamon leaf, cassia, Java citronella, origanum, thyme and neroli.

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[1]) *Atti R. Accad. dei Lincei, Roma* (5), **23** (1914), I. 439; *Chem. Zentralbl.* **1914**, II. 476. — [2]) *Feldärztl. Beil. d. Münch. med. Wochenschr.* **1915**, 68; *Apotheker Ztg.* **30** (1915), 39. — [3]) *Pharm. Ztg.* **60** (1915), 55. — [4]) *Deutsche med. Wochenschr.* **1915**, 285; *Apotheker Ztg.* **30** (1915), 135. — [5]) *Perfum. Record* **5** (1914), 99.

Preserving effect of essential oils.

As stated on page 131 of our *Report* of April **1913**, J. L. Rippetoe and L. E. Wise studied the development of mould fungi in glucose or sugary peptone solutions in the presence of various essential oils, in order to investigate the preserving influence of these. For the same purpose, C. B. Cochran and J. H. Perkins[1]) examined the action of different essential oils on the fermentation caused by yeast in cane sugar and glucose solutions. The results are given in the form of tables. For this reason, it is not easy to give a summary of the work, so that we must refer the reader to the original for particulars.

Destruction of typhoid fever bacilli through essential oils.

In the course of their investigations on killing typhoid bacilli in the organism of rabbits, E. Hailer and E. Ungermann[2]) tried the destructive action of some essential oils or their constituents on bacteria. The preparations were applied partly *per os*, partly *per rectum*, in some isolated cases also intravenously and intraperitoneally. Thymol proved to be efficacious; carvacrol, phenetole and anethole, on the contrary, ineffective. Terpine hydrate, borneol, citronellal, carvone and cineol possessed a remarkable influence on typhoid bacilli in rabbits; pinene, carvene, linalool, terpineol, camphor and camphoric acid did not make the virus disappear. Turpentine, juniper and peppermint oils showed no influence on the infection, whereas Ceylon cinnamon oil, if applied through the rectum, and sandalwood oil, when introduced through the stomach, killed the typhoid bacilli in the organism of rabbits.

Haemolytical action of terpenes.

For the sake of completeness, we would mention a treatise by N. Ishizaka[3]) on the haemolytic action of terpenes and the relation between chemical constitution and action. If the substances are classified according to their solubility (terpenes, terpene alcohols and terpene ketones), one notices that in the most closely allied, chemically speaking, the reduction of the surface tension of equimolecular solutions shows inverse proportions, *i. e.* the smaller the solubility, the greater the reduction of the surface tension. This rule does not hold good if there are certain differences in the chemical construction.

If the constitution is otherwise the same, unsaturated compounds are more readily soluble than saturated ones. The double linking in the carbonyl group is of similar importance for the solubility as the ethylene linking. The great solubility of carvone, compared with that of dihydrocarvone and carvotanacetone, explains itself by the connection of a double linking and a carbonyl group by means of the CH group. The same occurs in menthenone. The degree of haemolytic action of terpene derivatives proved to be dependent upon the purely physical properties, *e. g.* upon the alcoholic or ketonic nature. Some of the substances investigated, and unsaturated more than saturated ones, changed the blood-pigment into methaemoglobin. With alcohols and camphor there was no action at all, it was feeble with menthone, a little stronger with tetrahydrocarvone, dihydrocarvone and carvotanacetone, fairly strong with carvone and strongest with carvenone and menthenone. As for hydrocarbons, menthane and cymene did not cause any indication of haemolysis. Terpinene showed a considerable haemolytic power with the formation of methaemoglobin.

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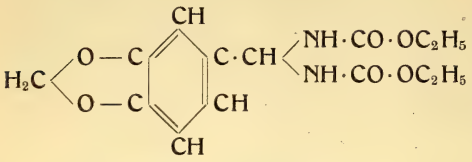
[1]) *Journ. Ind. Eng. Chemistry* **6** (1914), 304, 306. — [2]) *Arbeiten a. d. Kaiserl. Ges. Amt* **47** (1914), 303. — [3]) *Arch. f. exp. Pathol. u. Pharmakol.* **75** (1914), 194; *Chem. Zentralbl.* **1914**, I. 1292.

Piperonylidene *bis*urethane as hypnotic.

According to G. Bianchi[1]), piperonal (heliotropin) is physiologically speaking a substance of little efficacy and which, if administered to rabbits, is secreted in their urine partly unchanged, partly as piperonylic acid. The hypnotical action of piperonylidene bisurethane[2]) depends probably on the presence of ethyl groups and of the two carbonyls. The preparation is dissociated in the organism into ethylurethane, piperonal and piperonylic acid; it promotes the formation of superfluous urea and of two conjugated glucoronic acids, one of which contains the residue of the ethylurethane; the other, that of the piperonal. The presence of either substance in the urine can easily be proved.



Piperonylidene bisurethane.

Use of synthetic camphor for medicinal purposes.

Whereas the chemical industry can make itself quite independent from other countries by using synthetic camphor, one cannot avail oneself of this advantage as far as the supply of medicines is concerned, for the German Pharmacopoeia prescribes the exclusive use of the natural product of the camphor tree[3]).

E. Deussen[4]) is of the same opinion, as far as the internal use of synthetic camphor is concerned. He points out that the pharmacological action of the two kinds of camphor is different, as was proved at the time by Langgaard and Maass[5]). Furthermore, *l*-camphor is about 13 times more poisonous than *d*-camphor, as stated by Bruni[6]). It must here be remembered that inactive camphor is composed of equal parts of *d*- and *l*-camphor. Deussen is of opinion that artificial camphor may be used therapeutically for external purposes, but he thinks it rather daring to apply it in subcutaneous injections.

In order to decide this question, the Prussian Scientific Committee for Medical Affairs has been called upon by the Home Secretary to pronounce an opinion as to whether there are objections against the use of artificial camphor in tending sick people.

Prof. Dr. Heffter[7]) shares in his verdict Deussen's opinion. He mentions *e. g.* that the same phenomena as with camphor have been noticed with suprarenine, in that the *l*-suprarenine occurring in the suprarenal gland shows a very distinct action on the blood vessels, of which *d*-suprarenine is void, whereas *i*-suprarenine stands in between. It was true that, from the results of the experiments made with animals, only quantitative differences in the action might be deducted, but they alone did not entitle us to replace natural camphor without more ado by the artificial product for medicinal purposes. On the contrary, experiences as to the effect of artificial camphor in the treatment of human beings ought to be exacted first. On this point, however, literature fails us altogether. Only in the above-mentioned paper by Langgaard and Maass, it is said at the end that Grawitz tried artificial in the place of natural camphor, at the

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[1]) *Chem. Ztg.* **38** (1914), 1112. — *Boll. Chim. Farm.* **53** (1914), 324; *Chem. Zentralbl.* **1915**, I. 166. — [2]) Comp. *Report* October **1913**, 144. — [3]) *Pharm. Ztg.* **59** (1914), 734. — [4]) *Ibidem* 823. — [5]) *Therap. Monatsh.* **20** (1907), 573; *Report* April **1908**, 176. See also J. Hämäläinen, *Skand. Arch. f. Physiol.* **21** (1968), 64; *Report* April **1909**, 113. — [6]) *Gazz. chim. ital.* II. **38** (1908), 1; *Report* November **1908**, 161. — [7]) *Vierteljahresschr. f. gerichtl. Med.* III. **49** (1915), 1; *Pharm. Ztg.* **60** (1915), 6; *Apotheker Ztg.* **30** (1915), 10.

Charlottenburg hospital, and that no difference had shown itself, neither when given externally, nor internally. Owing to the complete absence of definite and minute clinical observations, Heffter thinks it rather risky to substitute artificial camphor straight away, for internal and subcutaneous applications, to the natural product, the use and dosage of which have become familiar to our physicians through many years of experience. He considers it desirable to examine systematically the possibility of using artificial camphor clinically as a stimulant for the blood circulation and respiration. He finds no objection against artificial camphor in preparations for external use.

According to R. Kaufmann[1]), inactive synthetic camphor is not only equal to Japanese camphor for external use, but even somewhat superior in efficacy. As further advantages, comparing it with the natural product, he mentions its purity, its deodorizing action and its present cheap price.

As Fröhner[2]) established through therapeutical experiments, already in 1908, there is no objection against the administration of camphor to horses. He therefore recommended at the time artificial camphor as a substitute for the natural product. According to Fröhner, objections against its application to human beings are unfounded.

Needless to say that camphor used for therapeutical purposes should fulfil certain distinct requirements as to purity. According to E. Richter[3]), the following impurities come into consideration: bornyl chloride, camphene, borneol, *iso*borneol and alcohol. Camphene makes itself conspicuous perhaps by lowering the m. p. The presence of bornyl chloride, even if the content is as low as 0,5 p. c., can be proved by the test with a copper wire netting. Richter thinks it more difficult to establish the presence of borneol and *iso*borneol.

P. Bohrisch[4]) writes about the testing of officinal camphor for its identity. According to Lenz[5]), natural camphor, when heated with 38 p. c. hydrochloric acid, ought to give a red colour, which is more intense than that resulting with vanillin and hydrochloric acid. However, when trying Lenz's test, Bohrisch never obtained a cherry-red colour, but at most yellowish and dirty pinkish-yellow tints. On heating carefully with a freshly prepared solution of vanillin and hydrochloric acid (1:100), however, officinal camphor gave at 30° a yellow, at 60° a bluish green and at 75 to 80° an indigo colour. The latter remained for several hours after cooling. Synthetic camphor gave a yellow colour when treated in the same manner.

With vanillin and sulphuric acid, camphor showed colours passing from pink into green and indigo. Synthetic camphor first became yellow; then it discoloured, and the mixture became turbid at the same time.

Supersan. In the treatment of pneumonia, pleuritis and bronchitis, Berliner[6]) obtained favourable results with gluteal injections of a mixture of menthol and eucalyptol, especially if antifebrin and salipyrin were added. This new remedy he called supersan.

As to an attempt to explain the antidotal action of turpentine oil in cases of phosphorus poisoning see page 45.

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[1]) *Feldärztl. Beil. d. Münch. Med. Wochenschr.* **1915**, 319; *Apotheker Ztg.* **30** (1915), 123. — [2]) *Pharm. Ztg.* **60** (1915), 24. — [3]) *Apotheker Ztg.* **30** (1915), 14. — *Pharm. Ztg.* **60** (1915), 46. — [4]) *Pharm. Zentralh.* **55** (1914), 1003. — [5]) *Arch. der Pharm.* **249** (1911), 286. — [6]) *Deutsche med. Wochenschr.* **1914**, 2100; *Apotheker Ztg.* **29** (1914), 988.

Phyto-physiological Notes.

Occurrence of resins and essential oils in plant tissues.

In a combined article on micro-chemistry and the biology of vegetal matter, O. Tunmann[1]) discusses the occurrence of resins and essential oils in plant tissues[2]). The essential oils mostly accompany the resins and act as solvents. In the resiniferous glands often only resins or only essential oils occur. A separation of resin and essential oil can be effected by A. Meyer's boiling and evaporation process, or by micro-distillation. Resins are recognized either by means of solvents or through copper salts; essential oils, through acids, as well as through Zimmermann's osmic acid test, after the cuttings have previously been treated with Javelle water, in order to destroy the tanniferous substances, &c. Fatty substances, which very frequently occur in resinous secretions, are recognized by means of their myeline forms.

Many resins and essential oils which the chemist has to deal with do not agree in various respects with those in the secretion cells. Chemistry alone can here do but little, and micro-chemistry must come to the rescue. It has thus been found that the stearoptene of Bulgarian otto of roses originates from the layers of membrane of epidermis cells, which have become cutaneous. Stearoptene is therefore not a constituent of the oil in the living tissue. Tunmann arrived at this result through micro-chemical investigations of the sublimates of *Rosa* and *Adiantum*, whereas Tschirch came to the same conclusion through chemical examination.

Tunmann turns against Giglioli's indication that essential oils make the cell membranes permeable for substances which otherwise cannot interchange by osmosis. He also criticizes Charabot's[3]) work and especially condemns his opinion that the essential oils are consumed during fertilization and seed formation.

The author further points out that plants containing essential oils generally are such as require much sunshine, frequently representatives ot the Mediterranean flora. Whereas according to some authors the content of essential oils in plants decreases from South to North, Schübeler quite generally presumed an increase of aromatic substances from South to North. Delpy and Hartwich found a larger number of oil glands on the leaves of *Lavandula, Marrubium* and *Melissa* of northern zones, whereas with *Rosmarinus, Thymus, Salvia, Hyssopus* and *Origanum* they were more numerous in plants of southern stations.

According to Tyndall, the plants surround themselves with a layer of vaporous essential oils, thus protecting themselves against excessive heating through the sunshine by day, as well as against too much cooling by night. It is true, objections against this view have been raised by Detto[4]).

The glands of *Myrtaceae* and *Rutaceae*, which are provided with arrangements for evacuation, are, as Haberland says, means of protection against aggressive animals; we find similar protective weapons in animal life (musk-deer, &c.).

More recent investigations have shown that one has to distinguish between resin glands, oil glands, starch glands and mucus glands and that the manner in which they partly or completely emit their secretions is closely connected not only with the chemical nature of these secretions, but likewise with their biological function.

Alkaloids, vegetal mucous and glucosides are also minutely discussed in the article.

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[1]) *Berichte d. deutsch. pharm. Ges.* **24** (1914), 262. — [2]) Comp. *Report* April **1909**, 118. — [3]) Comp. *Report* April **1900**, 50; April **1905**, 90; October **1905**, 89; April **1906**, 104; October **1906**, 106; April **1907**, 127; October **1907**, 136; November **1908**, 162. — [4]) Comp. *Report* October **1903**, 82.

Determination in plants of some glucosides hydrolysable by emulsin.

E. Bourquelot and his collaborators have again published some papers on the action of the emulsin enzymes and the occurrence in plants of glucosides hydrolysable by emulsin[1]).

Through the action of emulsin on anisyl alcohol dissolved in acetone, Bourquelot and Ludwig[2]) obtained *β*-anisyl glucoside, an odourless mass, which, in anhydrous state, melts at 137 to 138° on Maquenne's block. This glucoside possibly occurs in vanilla beans.

Together with Bridel, Bourquelot[3]) describes the determination of glucosides, hydrolysable by means of emulsin, in the orchids *Aceras anthropophora,* R. Br.; *Loroglossum hircinum,* Rich.; *Orchis purpurea,* Huds.; *O. Morio,* L.; *O. maculata,* L.; *O. latifolia,* L. and *O. conopsea,* L. As to the nature of these glucosides, the authors have nothing further to communicate as yet.

Finally, Bourquelot and Bridel[4]) report on the fermentative equilibrium and the specific action of enzymes, as regards their synthesizing properties.

Occurrence of mustard oils in some *Cruciferae.*

In order to prove the presence of mustard oils in some *Cruciferae,* J. J. Blanksma[5]) prepared combinations of these bodies with ammonia and phenylhydrazine. He distilled with steam the minutely powdered herb of *Cochlearia officinalis,* L., which had previously been treated with water, thus obtaining from flowers 0,062 p.c., from leaves 0,009 p.c., from the stalks 0,004 p.c., and from the whole plant 0,0305 p.c. of *d-sec.*-butyl mustard oil. With phenylhydrazine in hot alcohol, it forms phenyl-*d-sec.*-butyl-thiosemicarbazide, melting at 135°; with methylphenylhydrazine, 1-methylphenyl-4-*d-sec.*-butylthiosemicarbazide, melting at 112°.

From the herb of *Cochlearia danica,* L. only 0,006 to 0,007 p.c. of volatile oil was obtained, which consisted in the main of *d-sec.*-butyl mustard oil. Lady's smock (*Cardamine pratensis,* L.) yielded on distillation 0,00135 p.c. of oil, which proved to be *d*-butyl mustard oil. The yield from *Cardamine hirsuta,* L. was still smaller; this mustard oil could not be identified for certain, however.

Shepherd's purse (*Capsella Bursa pastoris,* Mnch.) did not, on steam distillation, yield any mustard oil, but a mercaptane.

Tropaeolum seeds *(Tropaelum majus)* contain benzyl mustard oil, which with phenylhydrazine yields 1-phenyl-4-benzylthiosemicarbazide (m. p. 158°).

The distillates of *Lepidium campestre, Nasturtium amphibium* and *Draba verna* strongly hindered the development of yeast.

Allyl mustard oil from mustard seeds gave with phenylhydrazine phenylallylthiosemicarbazide, melting at 118°; with methylphenylhydrazine, the corresponding methyl compound (m. p. 90°).

Anemonin in Ranunculus japonicus.

In some *Ranunculaceae, f. i. anemoneae,* there occurs an acrid substance, anemonin, $C_{10}H_8O_4$, which volatilizes with steam and which was investigated many years ago by H. Beckurts[6]) and later on by H. Meyer[7]). Meyer established a formula for anemonin,

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[1]) Comp. *Report* April **1914**, 125. — [2]) *Journ. de Pharm. et Chim.* VII. **9** (1914), 542. — [3]) *Ibidem* VII. **10** (1914), 14. — [4]) *Ibidem* VII. **9** (1914), 230, 603. — [5]) *Pharm. Weekbl.* **51** (1914), 1383; *Apotheker Ztg.* **29** (1914), 950; *Chem. Zentralbl.* **1915**, I. 262. — [6]) *Arch. der Pharm.* **230** (1892), 182. — [7]) *Monatsh. f. Chem.* **17** (1896), 283; **20** (1899), 634; *Chem. Zentralbl.* **1896**, II. 303; **1899**, II. 780.

which shows a great similarity to that of *iso*cantharidin. In consequence anemonin ought to have only one double linking. This is however, not the case. J. Asahina[1]) reduced the substance and in this way established with certainty the presence of two double linkings. In order to obtain anemonin, he distilled with steam the fresh herb of *Ranunculus japonicus*[2]), which abounds everywhere in Japan. From 10 kilos of fresh herb he obtained on an average 12 g. = 0,12 p. c. of a yellow oil, which violently attacks the mucous membranes and causes blisters to form. If the oil is left standing in the cold, crystals separate gradually from it, which show all the properties of anemonin, only that after recrystallization from alcohol or chloroform they do not melt at 152°, but only at 157 to 158°. When heating further, the substance congeals at 180° to a white mass with a feeble separation of gases and slowly decomposes at over 300°, turning brown. The mother lye of anemonin becomes gradually turbid and congeals to a mixture of insoluble flakes and prismatic crystals. The crystals are composed of a clear, transparent part, anemonin, and an opaque part, which melts only at about 300°, becoming charred in the process. By shaking anemonin suspended in glacial acetic acid with platinum black in an atmosphere of hydrogen, Asahina obtained tetrahydroanemonin (m. p. 155°). On further heating, the melted substance remains unchanged up to 290° and becomes charred at about 300° with the development of gases. The elementary analysis confirmed the formula $C_{10}H_{12}O_4$.

Volatile constituents of hornbeam leaves.

On page 138 of our *Report* of October **1912**, we have discussed a paper by Th. Curtius and H. Franzen on the volatile constituents of hornbeam leaves, which appeared at the time in the *Sitzungsberichte der Heidelberger Akademie der Wissenschaften* The same communications have now been published too in *Liebigs Annalen der Chemie*[3]).

In their 7th communication on the chemical constituents of green plants, the authors describe an attempt to synthesize the leaf aldehyde (α,β-hexenealdehyde)[4]). However, as they did not arrive at the desired result and only obtained some bodies which are of little interest for our special domain, we simply mention the paper.

Amygdalin in plum-kernels.

G. Kassner and K. Eckelmann[5]) proved the presence of amygdalin in plum-kernels in the usual way by extracting the material with alcohol, after it had been deprived of the fatty substances, and precipitation with ether.

The plum-kernels contained 42,92 p. c. of fatty oil.

The reduction of aldehydes by means of yeast has been discussed on page 91 of this *Report*.

Chemical Notes.

A. Brochet and M. Bauer[6]) describe the reduction of aliphatic ethylene linkings with the aid of nickel under moderate pressure. Methyl cinnamate, mixed with methyl

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[1]) *Berl. Berichte* **47** (1914), 914. — [2]) The *Index Kewensis* distinguishes between *Ranunculus japonicus*, Langsd. = *R. Langsdorfii*, Spreng. and *R. japonicus*, Thunb. = *R. acris*, L. Asahina does not indicate the author's name. — [3]) *Liebigs Annalen* **404** (1914), 93. — [4]) *Sitzungsber. der Heidelberg. Akad. der Wissensch.* Class for Mathem. and Nat. Science, Sect. A, **1914**, 22. Treatise. Heidelberg 1914. — [5]) *Arch. der Pharm.* **252** (1914), 405. — [6]) *Compt. rend.* **159** (1914), 190. Details as to method and apparatus are found in a treatise previously published by Brochet (*Bull. Soc. chim.* IV. **15** [1914], 554).

alcohol and activated nickel, was thus reduced already in the cold with formation of methylphenyl propionate (b. p. 237 to 238°). From 60 to 80° anethole yielded *p*-methoxypropylbenzene. Eugenol, safrole and *iso*eugenol were likewise reduced, *iso*-eugenol giving the same reduction-product as eugenol.

In their 8th communication on synthesis in organic chemistry, E. Paternò, G. Chieffi and G. Perret[1]) describe some experiments, which we intend mentioning briefly. Acetophenone and benzyl alcohol yielded on exposure to the light α,β-diphenylpropane glycol, an oil of light yellow colour. Only small quantities of hydroanisoin could be isolated from the products obtained by exposing anisaldehyde and toluene to the light; saligenin and benzophenone gave only benzopinacone, in addition to the unaffected part of the original material, whereas saligenin and acetophenone probably yielded salireton, $C_{14}H_{12}O_3$. With toluene as well as with acetophenone heliotropin (piperonal) forms colourless crystals melting at 226 to 228°.

In a series of articles, E. Erlenmeyer[2]) deals with the activation of cinnamic acid and benzaldehyde by asymmetric induction, *i. e.* by boiling the substances in buestion with an alcoholic solution of tartaric acid. He believes that in this way he can obtain optically active cinnamic acid and optically active benzaldehyde. As for benzaldehyde, E. Wedekind[3]) is of opinion that the alleged activation is to be explained by an optically active impurity, presumably a kind of acetal combination of tartaric acid with benzaldehyde.

Phosphorites and phosphorates.

In a treatise on the behaviour of unsaturated compounds towards phosphorus and oxygen, R. Willstätter and E. Sonnenfeld[4]) describe a new class of compounds, which they call phosphorites and phosphorates, because they are built up in an analogous way as nitrosites and nitrosates. They form on shaking the solutions of unsaturated compounds (amylene, menthene, pinene, cinnamates, &c.) in benzene or *cyclo*hexane under the exclusion of moisture with finely divided white phosphorus. For this purpose the authors constructed a special shaking apparatus, which is connected with an oxygen generator. The double linking thus takes up P_2O_4, with the exception of that of allyl alcohol, which yielded a combination of the formula $(C_3H_4O)_3P_4O_6$. The speed of the reaction slackens suddenly after the absorption of three atoms of oxygen, the fourth atom being added about six times more slowly. If the reaction is interrupted, *e. g.* that of 1 molecule of *cyclo*hexane with 2 atoms of phosphorus after 3 atoms of oxygen have been absorbed, one finds that a product of the formula $C_6H_{10}P_2O_3$, a phosphorite, has formed; on further absorption of oxygen, the phosphorate, $C_6H_{10}P_2O_4$, results.

In this way pinene furnishes pinene phosphorate, $C_{10}H_{16}P_2O_4$, a slightly yellow, crystalline, remarkably hygroscopic substance of a not unpleasant odour, reminding of fir resin. It still remains to be ascertained whether the compound described by Sieburg[5]) as terpenol hypophosphorous acid is identical with it. Menthene forms a phosphorate, $C_{10}H_{18}P_2O_4$, a yellowish white, fairly hygroscopic powder. Cinnamic acid ester reacts with phosphorus and oxygen as violently as the unsaturated hydrocarbons.

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[1]) *Gazz. chim. ital.* **44**, I. (1914), 151; *Chem. Zentralbl.* **1914**, I. 2150. — [2]) *Biochem. Zeitschr.* **64** (1914), 296, 366, 382; **66** (1914), 509; *Chem. Zentralbl.* **1914**, II. 1230. — [3]) *Berl. Berichte* **47** (1914), 3172. — [4]) *Berl. Berichte* **47** (1914), 2801. — [5]) *Biochem. Zeitschr.* **43** (1912), 280; *Report* April **1913**, 98.

Hydrocarbons.

The synthesis of some hydrocarbons, allied to the terpenes, has been described by W. N. Haworth and A. W. Fyfe[1]). By condensing *d*-1-methyl-*cyclo*hexane-3-one with ethyl cyanoacetate, they obtained *l*-1-methyl-Δ^2- and -Δ^3-*cyclo*hexene-3-cyanoacetic acids and their ethyl esters. The elimination of carbon dioxide by the distillation of the cyano-acids leads to a mixture of *d*-1-methyl-Δ^2- and -Δ^3-*cyclo*hexene-3-acetonitrile. The action of magnesium methyl iodide on these nitriles leads to *d*-1-methyl-3-acetonyl-Δ^2- and -Δ^3-*cyclo*hexene, which distinguish themselves from one another by the solubility of their semicarbazones. By bringing together these ketones and magnesium methyl iodide, the authors obtained *d*-1-methyl-3-*iso*butanol-Δ^2- and -Δ^3-*cyclo*hexene, from which *d*-1-methyl-3-dimethylvinyl-Δ^2- and -Δ^3-*cyclo*hexene resulted by dehydration. The dehydration of *d*-1-methyl-3-*iso*butanol-Δ^3-*cyclo*hexene by means of potash hydrogen sulphate led to a hydrocarbon, which smells of limonene and presumably has a different composition from the hydrocarbon obtained with the aid of oxalic acid. In the same manner Δ^1-*cyclo*hexene-1-acetonitrile was converted into 1-acetonyl-Δ^1-*cyclo*hexene, which with magnesium methyl iodide yields the terpene alcohol 1-*iso*butanol-Δ^1-*cyclo*hexene (b. p. 106° at 17 mm.; $d_{4^\circ}^{20^\circ}$ 0,9258; m. p. of the phenylurethane = 105°), which under separation of water passed into the terpene 1-dimethylvinyl-Δ^1-*cyclo*hexene (b. p. 172 to 173°; $d_{4^\circ}^{20^\circ}$ 0,8537; n_D 1,4854). In this case too, the dehydration by means of potash disulphate led to a different hydrocarbon.

Oxidation of hydrocarbons.

As is known, only the unsaturated hydrocarbons are oxidized out of a mixture of unsaturated and saturated hydrocarbons, which latter are thus purified. N. Kishner[2]) studied this reaction more closely and found that it is a real induced reaction which takes place, as, in consequence of the oxidation of the unsaturated hydrocarbon, the saturated hydrocarbon is rather strongly attacked, which is not the case to such an extent with the pure hydrocarbon. 2,6-dimethyloctane *f. i.* is fairly stable when being boiled with potassium permanganate, but if menthene is added, the octane is likewise oxidized already at 50°.

We made a similar observation at the time, when determining cineol with a potassium permanganate solution (comp. page 71). Pure cineol is scarcely acted upon in the cold by potassium permanganate, whereas in mixtures with easily oxidizable substances, such as terpineol, it is partly attacked. It is different as regards pinene, which is easily oxidized, but in the presence of cineol it becomes fairly stable against the action of potassium permanganate solution[3]).

Isoprene. Some time ago we described an isoprene lamp, constructed by Harries and Gottlob[4]), with the aid of which only about 1 p.c. of pure isoprene were obtained from pinene, as against 50 p.c. from commercial carvene (limonene). At the time Harries and Gottlob supposed that the formation of isoprene from turpentine oil was due to the presence of dipentene.

According to H. Herty and J. O. Graham[5]), this idea is not correct, for when preparing isoprene from turpentine oil with the aid of the isoprene lamp, they obtained

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[1]) *Journ. chem. Soc.* **105** (1914), 1659. — [2]) *Journ. russ. phys. chem. Ges.* **45** (1913), 1788; *Chem. Zentralbl.* **1914**, I. 1498. — [3]) *Report* April **1913**, 63. — [4]) Comp. *Report* October **1911**, 127. — [5]) *Journ. Ind. Eng. Chemistry* **6** (1914), 803.

in all 5,5 p.c. of isoprene. The fraction boiling at 155 to 156° (pinene fraction) yielded 8 p.c.; that boiling at from 169 to 175°, 0,5 p.c. and the fraction boiling above 175°, 0 p.c. of isoprene. As may be seen, the last fractions, which, according to their b. p., might contain dipentene, furnished little or no isoprene. Herty and Graham further heated in the isoprene lamp the turpentine oil from *Pinus serotina*[1]). In accordance with its high content of limonene, it yielded 12 p.c. of isoprene. Pine oil, which chiefly consists of terpineol, yielded 4 p.c. of isoprene.

Finally an oil was investigated, which is obtained as a by-product in blowing off the digestors in the manufacture of wood pulp from spruce fir. It boiled in the main between 171,3 and 174,9° ($d_{15°}$ 0,8639; n_D 1,4916) and consisted chiefly of cymene. Isoprene was not obtained from this product.

Camphene. Through the action of dilute aqueous hypochlorous acid on camphene, G. G. Henderson, I. M. Heilbron and M. Howie[2]) obtained a chlorohydrin $C_{10}H_{16}Cl \cdot OH$, melting at 93°. It reacts with aqueous and alcoholic solutions of potassium hydroxide forming *iso*camphenylanaldehyde, and furnishes camphene dichloride with phosphorus pentachloride. When treating the chlorohydrin with zinc and alcohol, *iso*borneol is formed, which shows that the chlorohydrin is identical with chloro*iso*borneol. When oxidized with chromic acid, it is converted into a crystalline chloroketone, $C_{10}H_{15}OCl$ (m. p. 132°), which on heating with zinc and alcohol yields camphor.

Regarding the constitution of fenchene, see page 95.

Limonene. On page 137 of our *Report* of October **1911**, we discussed a paper by G. Vavon on the reduction of limonene. Detailed communications about this investigation have meanwhile been published by the author elsewhere[3]). The *d*-carvomenthene (dihydro-limonene) obtained synthetically through the action of water on the magnesium derivative of limonene monohydrochloride has a lower rotation (α_{578} + 59 and + 89°; α_{436} + 117 and + 175°) than the product (α_{578} + 97,3°; α_{436} + 193°)[4]), resulting from the reduction of *d*-limonene. Vavon does not say anything as to the other properties of the synthetic product. Carvomenthene, obtained by reducing limonene, forms with hydrogen chloride a hydrochloride, $C_{10}H_{19}Cl$, boiling at 85 to 86° (13 mm.), 180 to 185° (ordinary pressure, partial decomposition); $d_{4°}^{21°}$ 0,934; $n_{D21°}$ 1,460.

In connection with this investigation, Vavon[5]) reports on the speed of the reaction in catalytical hydrogenations with platinum and on the exhaustion of the catalyst. If a sufficient quantity is used for reducing the limonene, the speed of the reaction remains almost constant during the whole process. If less platinum is taken, the reaction proceeds more slowly, and if still smaller quantities are used, the reaction remains incomplete, *i.e.* only the extracyclic double linking is reduced. Heating to a very high temperature reduces the activity of platinum, so that only easy reductions can be executed with its aid, such as those of the extracyclic double linking of limonene.

As will be remembered, A. Blumann and O. Zeitschel[6]) isolated from resinified turpentine oil the alcohol verbenol and the ketone verbenone. Both bodies must have formed through autooxidation of pinene, which oxidation takes place in an abnormal

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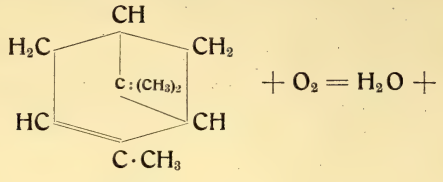
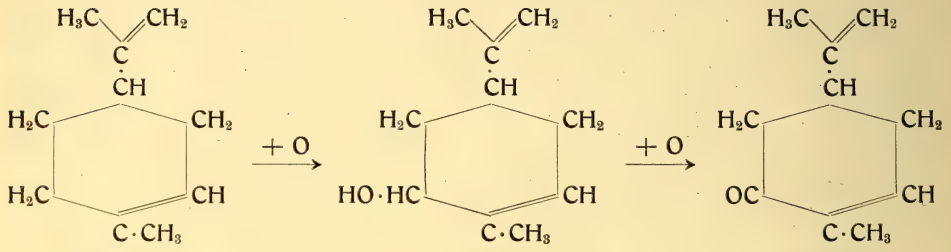
[1]) Comp. *Report* November **1908**, 120. — [2]) *Journ. chem. Soc.* **105** (1914), 1367. — [3]) *Bull. Soc. chim.* IV. **15** (1914), 282. — [4]) The rotation refers to rays $\lambda = 578$ and $\lambda = 436$ of the mercury lamp. — [5]) *Bull. Soc. chim.* IV. **15** (1914), 287. — [6]) *Berl. Berichte* **46** (1913), 1178; *Report* October **1913**, 103.

way, in that the double linking is preserved, whereas a neighbouring methylene group is attacked. The autooxidation of limonene goes on in the same manner, as the same authors have recently discovered[1]). In this case too not the double linking, but a neighbouring methylene group is attacked, under the formation of the still unknown alcohol carveol and the ketone carvone.



α-Pinene. Verbenone.



Limonene. Carveol. Carvone.

For this investigation a carvene (limonene) was used, which had been purified by repeated fractionation over sodium: $d_{15°}$ 0,845; α_D + 106°. It remained for 2½ months in a losely covered vessel, exposed to the action of the oxygen of the air in the presence of a small quantity of water. After this time, the feebly acid reaction product was neutralized with soda solution, and the volatile constituents were distilled off with steam. It resulted that from 400 g. of carvene 270 g. of volatile products had formed. Through treatment with sulphite solution, *i*-carvone was isolated. The ketone which, after having been separated from the hydrosulphonic acid solution, had been purified by converting it into its semicarbazone (m. p. 154 to 155°), boiled at 230°; $d_{15°}$ 0,965. The part of the oil, which did not react with sulphite, was treated with benzoyl chloride and pyridine, and the alcohol recovered from the benzoate was purified by way of the phenylurethane (m. p. 94 to 95°). In this way pure *i*-carveol, $C_{10}H_{16}O$, a viscid oil of a not very pleasant odour, resembling that of dihydrocarveol, was obtained. b. p. 108 to 110° (11 mm.); 226 to 227° (751 mm.); $d_{15°}$ 0,9578; $\alpha_D \pm 0$; $n_{D18°}$ 1,4961. Genvresse's limonenol[2]) is most likely only an impure carveol. Genvresse indicates the following constants for the product: b. p. 135° (15 mm.); $d_{18°}$ 0,9669; $\alpha_{D17°}$ + 19°21′; n_D 1,497. Otherwise only one derivative of carveol was known, carveol methyl ether, which Wallach[3]) obtained from limonene tetrabromide by treating with alkalis and heating with sodium.

Blumann and Zeitschel ascertained the following properties for the acetate of *i*-carveol: m. p. 115 to 116° (10 mm.); $d_{15°}$ 0,9755. The ester has a pronounced spearmint odour. The phthalate melts between 136 and 137°. By oxidation with chromic acid in glacial acetic acid solution, *i*-carveol is converted into *i*-carvone. The dehydration

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[1]) *Berl. Berichte* **47** (1914), 2623. — [2]) *Compt. rend.* **132** (1901), 414; *Report* April **1901**, 66. — *Liebigs Annalen* **281** (1894), 127; *Report* October **1894**, 12.

with zinc chloride or dilute suphuric acid led to *p*-cymene; the addition of water by shaking with 5 p.c. sulphuric acid, to a hydrate, $C_{10}H_{18}O_2$, melting at 132 to 133°.

The fact that pure limonene, and especially that obtained from caraway oil, when exposed to the air, soon again takes the smell of the raw material, can easily be explained by the autooxidation of carveol into carvone.

Effect of high temperatures on sesquiterpenes.

Many experiments, carried out by F. W. Semmler and W. Jakubowicz[1]), have proved that it is possible to break down sesquiterpenes into terpenes, and probably, into isoprene. Isoprene cannot be determined as such, but its condensation products can. When breaking down *β*-gurjunene, the presence of terpinene could be proved. 10 g. of gurjunene were heated to 330° for about 12 hours in a sealed tube, when 12 p.c. of a substance were obtained, which boiled at from 60 to 65° (10 mm.) and was recognized as *α*-terpinene by means of its nitrosite (m. p. 154°). Further, in addition to unaltered gurjunene, dipentene was present, which had resulted presumably by the addition of primarily formed isoprene to gurjunene. On breaking down *α*-gurjunene, a terpene formed, of which no solid derivatives could be obtained. The fraction which boiled highest was a blue oil, representing perhaps an oxidation product of gurjunene. Similar blue oils have repeatedly been observed when distilling essential oils. On breaking down cedrene, it was likewise impossible to prove the presence of a terpene by means of solid derivatives. Caryophyllene furnishes perhaps a terpene allied to pinene as well as a diterpene; cadinene, presumably a monocyclic sesquiterpene.

F. W. Semmler and K. G. Jonas[2]) report on some derivatives of sesquiterpenes and diterpenene, as well as on synthetical experiments in this domain. On a former occasion[3]) they had obtained octahydro-*α*-camphorene, as a liquid boiling between 174 and 176° (9 mm.); n_D 1,46470. On repeated hydrogenation of *α*-camphorene, they now obtained an octahydro-*α*-camphorene boiling between 183 and 186° (14 mm.); $d_{20°}$ 0,8341; $\alpha_D \pm 0°$; n_D 1,46001.

They also report on the bicyclic diterpene *iso*-*α*-camphorene. If myrcene is polymerized, a diterpene fraction forms, which yields liquid products on being treated with gaseous hydrochloric acid. The authors succeeded, by elimination of hydrogen chloride, in arriving at a hydrocarbon, for which they propose the name of *iso*-*α*-camphorene. It was likewise possible to produce this body by inverting *α*-camphorene with sulphuric and glacial acetic acid. The constants of this diterpene are: b. p. from 193 to 197° (19 mm.); $d_{21°}$ 0,9029; $n_{D20°}$ 1,50300. The reduction with platinum and hydrogen furnished hexahydro*iso*-*α*-camphorene: b. p. 180 to 186° (14 mm.).

By heating *l*-*α*- and *d*-*β*-phellandrene, *α*-pinene, *β*-pinene, and limonene (the last-named in the presence of sulphuric and glacial acetic acids) in a sealed tube, diterpenes were obtained, which did not afford any solid addition products with hydrochloric acid. Some oxygenated terpene bodies, which were heated in a sealed tube, together with a dehydrating agent served for further synthesizing experiments. In this way *α*-camphorene formed from linalool; from citronellal, an oxide of the diterpene class, $C_{20}H_{34}O$, b. p. 190 to 200° (17 mm.). The reduction with platinum and hydrogen yielded the corresponding saturated body, $C_{20}H_{38}O$.

*Cyclo*isoprene-myrcene[4]) can be reduced by means of platinum and hydrogen to hexahydroisoprene-myrcene.

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[1]) *Berl. Berichte* **47** (1914), 2252. — [2]) *Berl. Berichte* **47** (1914), 2077. — [3]) Comp. *Report* October **1913**, 35. — [4]) Comp. *Report* October **1913**, 35.

It was further tried to synthetize cadinene. α- and β-phellandrene yielded sesquiterpenes of undoubtedly bicyclic nature when heated with isoprene in a sealed tube. The sesquiterpene obtained by condensing β-phellandrene with isoprene is presumably identical with β-santalene.

The condensation of limonene with isoprene can be started by means of ethylsulphuric acid. For this purpose limonene and isoprene in the proportion of 2:1 are slowly mixed under stirring with three times their quantity of ethylsulphuric acid, which has been cooled down to — 18°. The reaction begins suddenly with a considerable rise of temperature; after about 3 to 5 minutes, the product of the reaction is poured into water and furnishes after neutralization and distillation a sesquiterpene fraction boiling at from 120 to 127° (10 mm.).

Re Wallach's colour reaction of cadinene see page 25.

Caryophyllene. By heating an alcoholic solution of β-caryophyllene nitrosite, a hydrocarbon is formed which E. Deussen[1]) calls γ-caryophyllene, whereas he formerly named it *iso*caryophyllene[2]). γ-Caryophyllene boils at 124 to 125° (14 mm.); α — 22,22°. Following Paal's process, it can be reduced to γ-dihydrocaryophyllene (b. p. 124 to 124,5° at 12 3/4 mm.; $d_{21°}$ 0,8872; α_D — 29,41°; $n_{D21°}$ 1,4880).

Deussen further describes some halogen derivatives of β-caryophyllene nitrosite, *i. e.* the already known β-hydrochlorocaryophyllene nitrosite[3]) (from blue β-caryophyllene nitrosite and hydrochloric acid), β-bromocaryophyllene nitrosite, melting at 104 to 105° (from β-nitrosite and bromine in chloroform) and β-iodocaryophyllene nitrosite, from iodine and β-nitrosite in chloroform; m. p. 125°.

In the same treatise, Deussen mentions the action of sodium alcoholates on α-caryophyllene nitrosochloride. When α-caryophyllene nitrosochloride is treated with sodium methylate, α-methoxynitrosocaryophyllene results, which melts at 116°. Sodium ethylate and propylate cause hydrochloric acid to be split off from the nitrosochloride, when α-nitrosocaryophyllene is formed.

Besides, Deussen writes about the action of sulphuric acid on caryophyllene from clove oil and on alkoxy compounds of β-caryophyllene nitrosite and their optical rotation. He prepares said bodies by treating β-caryophyllene nitrosite with alcohols, in which caustic potash is dissolved. Ethoxynitrosocaryophyllene (m.p. 163°)[4]) has been described by him already some time ago.

Deussen also mentions a crystalline body which he obtained from the mother lye resulting from the preparation of β-caryophyllene nitrosochloride, and which formed yellow crystals melting at 168 to 169°. Its composition may probably be expressed by the formula $C_{13}H_{23}NO$.

He finally reports on the melting point of mixtures of α-caryophyllene nitrosobromide and α-bromocaryophyllene nitrosochloride, as well as on the nomenclature of optically active caryophyllene compounds.

As to the properties of gurjunenes and their derivatives see page 23.

The tricyclic sesquiterpene copaene has been described on page 14 of this *Report*.

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[1]) *Journ. f. prakt. Chem.* II. **90** (1914), 324. — [2]) K. Meyer, *Inaug.-Dissert.*, Leipzig 1912. — Deussen, *Copaivabalsame und ihre Verfälschung*, Leipzig 1914. — [3]) Comp. *Report* October **1912**, 149. — [4]) Comp. *Report* October **1912**, 149.

Azulene. The blue substance, to which some essential oils, such as Roman chamomile oil, wormwood oil, &c., owe their intense colour, has been closely investigated by A. E. Sherndal[1]). He calls it azulene, a name which was proposed already in 1864 by S. Piesse[2]). Azulene dissolves in concentrated mineral acids and separates unchanged when water is added. He shook 50 g. of an intensely blue fraction[3]) with 10 g. of 63 p.c. sulphuric acid and allowed the mixture to stand during the night. The acid layer was then decanted, diluted with water and treated with light petroleum, until this did not colour blue any more. The petroleum solution was then shaken with 85 p.c. phosphoric acid, until the blue colour had disappeared. The acid, which then showed a dark red colour, was decanted, diluted with water and extracted with ether, when 0,141 g. (0,28 p. c.) of a blue oil was obtained. In the same way, Sherndal prepared larger quantities of azulene, which he purified by distillation *in vacuo*. Pure azulene in a thin layer shows a dark blue colour; in thicker layers it looks black. It has a faint odour like phenol, recalling a little that of thymol. By combustion, as well as by ascertaining its molecular weight in benzene, the composition $C_{15}H_{18}$ was found. It resinifies quickly when exposed to the air. B. p. 295 to 300° (ordinary pressure) under partial decomposition, 185 to 195° (25 mm.); $d_{25°}$ 0,9738. It dissolves in most of the organic solvents. The solution in 60 to 65 p.c. sulphuric acid is yellow and fluoresces strongly; that in phosphoric acid fluoresces in reddish yellow and apple-green tints. From acid solutions, light petroleum does not take up any azulene, so that sesquiterpenes can easily be removed. Azulene remains unchanged when heated on the water-bath with 94 p.c. sulphuric acid. The action of nitric acid in acetic acid solution led to a yellow, amorphous mass. The oxidation with potassium permanganate did not afford any characteristic resolution products. Through the action of acetic anhydride and sulphuric acid a substance was obtained which dissolved in water and was most likely a sulphonic acid.

It seems that azulene is closely allied to the terpenes and contains several double linkings.

Sherndal points out that blue bodies have often been noticed in reactions of acids on essential oils, for example in the reaction of phosphorus pentoxyde on guayol, or also when heating gurjunene under pressure. He further mentions the well-known colour reactions with sulphuric and glacial acetic acids. It remains to be investigated whether azulene or allied bodies are formed in these reactions.

"Benzoterpenes" is the name given by F. W. Kay and A. Morton[4]) to terpene-like hydrocarbons, which are derived from tetrahydronaphthalene. Similar compounds have not been met with in nature so far, but they are of theoretical interest, as they are closely allied to the sesquiterpenes. The authors think that benzo-*p*-menthane is the basis of the benzoterpenes (I). In order to arrive at the benzo-nor-*p*-menthene, the authors proceed as follows: α-naphthonitrile is saponified to α-naphthoic acid, which is reduced by means of sodium and alcohol to tetrahydro-α-naphthoic acid (II). By brominating ethyl tetrahydro-α-naphthoate, ethyl α-bromotetrahydro-α-naphthoate (III) is obtained, from which hydrogen bromide is separated by treatment with diethylaniline, when ethyl Δ^1-dihydro-α-naphthoate (IV) is formed. Ethyl tetrahydro-α-naphthoate can be converted into benzo-nor-*p*-menthan-10-ol (V) with the aid of magnesium methyl iodide. It is a liquid of camphorlike smell and boils at 166° (30 mm.). By splitting

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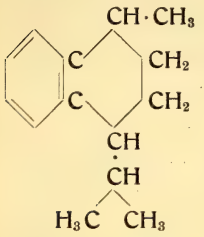
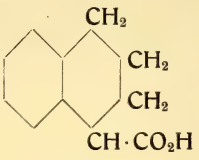
[1]) *Journ. Americ. chem. Soc.* **37** (1915), 167. — [2]) *Compt. rend.* **57** (1864), 1016. — [3]) Unfortunately the author does not indicate from what oil the fraction was taken. — [4]) *Journ. chem. Soc.* **105** (1914), 1565.

off water through potassium pyrosulphate, this alcohol is converted into benzo-$\Delta^{10(11)}$-nor-*p*-menthene (VI), which smells like cedrene and shows great indifference towards potassium permanganate; b. p. 259 to 261° (745 mm.) No nitroso compound was obtained. When heating the hydrocarbon with sodium alcoholate in a sealed tube, it is converted into benzo-$\Delta^{10(4)}$-nor-*p*-menthene. In the same way benzo-Δ^{3}-nor-*p*-menthen-10-ol (VII), m. p. 101 to 102°, forms from ethyl Δ^{1}-dihydro-α-naphthoate. It has an odour like naphthalene. By splitting off water by means of potassium pyrosulphate, benzo-$\Delta^{3,10(11)}$-nor-*p*-menthadiene (VIII) was obtained, b. p. 255 to 256°. After reduction it affords benzo-$\Delta^{10(4)}$-nor-*p*-menthene (see above).

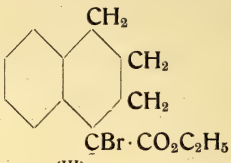


(I) Benzo-*p*-menthane.



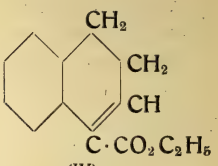
(II)

Tetrahydro-α-naphthoic acid.



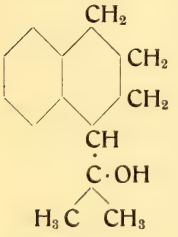
(III)

Ethyl α-bromotetrahydro-α-naphthoate.

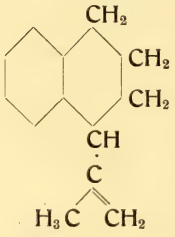


(IV)

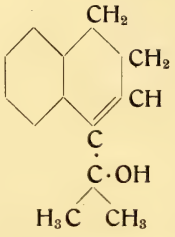
Ethyl Δ^{1}-dihydro-α-naphthoate.



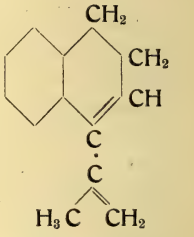
(V) Benzo-nor-*p*-menthan-10-ol.



(VI) Benzo-$\Delta^{10(11)}$-nor-*p*-menthene.



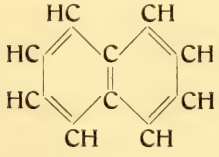
(VII) Benzo-Δ^{3}-nor-*p*-menthen-10-ol.



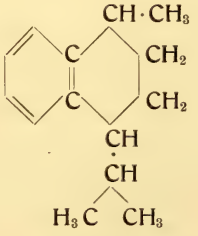
(VIII) Benzo-$\Delta^{3,10(11)}$-nor-*p*-menthadiene.

Furthermore the preparation of α-naphthyldimethyl carbinol and α-*iso*propenyl-naphthalene is described.

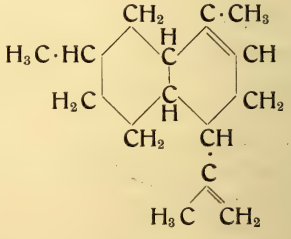
The relationship of *p*-benzo-*p*-menthane to the sesquiterpenes is to be seen in the following scheme:—



Naphthalene.



Benzo-*p*-menthane.



α-Selinene[1]).

Styrene. The fact that pure styrene does not change spontaneously into meta-styrene ought, according to H. Stobbe[2]), to lead to the supposition that an equilibrium would finally result in such homogeneous systems, *i. e.* that every polymerization was

[1]) Comp. *Report* April **1913**, 138. — [2]) *Berl. Berichte* **47** (1914), 2701.

counteracted by a depolymerization. In order to examine this question, solutions of styrene and metastyrene in benzene were made, half being kept in the dark the other half being exposed to the sunlight for two months. The exposed solutions of styrene showed an increase of the index of refraction, which indicated the formation of metastyrene. The decrease of the values in the exposed metastyrene solutions pointed to the formation of styrene. The solutions kept in the dark had remained unchanged. It was easy to determine that these reactions had really taken place. When alcohol was added to the exposed solution of styrene, metastyrene was precipitated. The exposed solution of metastyrene, which had become very liquid, discoloured potassium permanganate solution, whereas the metastyrene solution, which had been kept in the dark, did not react on it. It follows that both solutions strive for an equilibrium: monomeride $\rightleftarrows$ polymeride.

Alcohols.

Basic properties of oxygen in alcohols.

In a series of treatises on the high valencies of organic compounds, W. Tschelinzew[1]) reports on the basic properties of oxygen in aromatic alcohols as well as in alcohols of the terpene series and on the relationship between principal and accessory valencies in alcohols. As regards details, we must refer the reader to the original. We would mention only that some magnesium alcoholates are described: that of benzyl alcohol forms a solid, sticky mass, whereas that of cinnamyl alcohol is a crystalline powder. Menthol, terpineol and *d*-borneol form white, crystalline magnesium alcoholates.

B. Mereschkowsky[2]) has something to report on the actions of anhydrous boric acid on alcohols of the terpene series, when acid esters are formed, which decompose later on into boric acid and unsaturated hydrocarbons. In this way, menthol afforded Δ^2-menthene, in addition to small quantities of Δ^3-menthene and $\Delta^{4(8)}$-menthene. The ozonization of Δ^2-menthene led in the main to α,α-methyl*iso*propyladipic acid, α,α-methyl-*iso*propyladipic acid aldehyde, acetone, and a large number of polymerization products. Through the action of boron trioxide on dihydrocarveol, a mixture of two compounds is formed, perhaps limonene and *iso*limonene. Tetrahydrocarveol and boric acid anhydride chiefly yield Δ^2-menthene.

Geraniol. Through the action of thionyl chloride on geraniol in the presence of pyridine, M. O. Forster and D. Cardwell obtained a chloride, which may be considered as geranyl chloride and is identical with the chloride which J. Dupont and L. Labaune found after having treated linalool or geraniol with hydrogen chloride[3]). As Dupont and Labaune[4]) now say, they tried the thionyl chloride method already at the beginning of their experiments and ascertained that it gave good results with linalool, whereas geraniol afforded derivatives which, when distilled, showed sulphur compounds in the last fractions.

They have further been able to convince themselves again that the reaction of alkalis on geranyl chloride chiefly produces linalool.

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[1]) *Journ. russ. phys. chem. Ges.* **45** (1913), 1904, 1912, 1917; *Chem. Zentralbl.* **1914**, I. 1823, 1826, 1827. — [2]) *Journ. russ. phys. chem. Ges.* **45** (1914), 1686; *Chem. Zentralbl.* **1914**, I. 1425. — [3]) Comp. *Report* October **1913**, 139. — [4]) *Berichte von Roure-Bertrand Fils* April **1914**, 3.

Linalool. Some years ago, Enklaar[1]) obtained 2,6-dimetyloctanol-6 in addition to 2,6-dimethyloctane, when reducing linalool with nickel and hydrogen, which speaks in favour of the formula for linalool, established by Tiemann and Semmler. P. Barbier and R. Locquin[2]) feared that molecular transpositions might occur during the reduction with nickel and hydrogen. They therefore reduced linalool with platinum and hydrogen, which process goes on at a low temperature. They used linalool obtained from linaloe oil by fractionated distillation and which showed the following constants: b. p. 87 to 89° (13 mm.); $d_{4^\circ}^{0^\circ}$ 0,888; $[\alpha]_{D17^\circ}$ — 14,5°. 2,6-dimethyloctanol-6 was obtained as product of the reaction. It easily splits off water, forming 2,6-dimethyloctene-6,7, and is identical with the 2,6-dimethyloctanol-6, which Barbier and Locquin prepared from methyl-*iso*hexylketone and magnesium ethyl bromide. Enklaar likewise obtained the alcohol synthetically, but he started from methylheptenone, which according to Barbier and Locquin is easily disposed to undergo molecular transpositions when treated with magnesium alkyl haloids. Tetrahydrolinalool, obtained by reduction from linalool, boiled at from 86 to 88° (10 mm.) and showed $[\alpha]_D$ — 0° 24'. The allophanate of this tetrahydrolinalool melted at 88°; the synthetical product, at 110 to 111°. The authors explain this difference as regards the melting point by the small refraction of tetrahydrolinalool. The allophanate of tetrahydrolinalool, which was obtained by reduction of *i*-linalool, melted likewise at 110 to 111°.

*Methyl*cyclo*hexanol.* Following up his former papers on synthetic glucosides[3]), J. Hämäläinen[4]) reports on the preparation of glucosides from isomeric methyl *cyclo*hexanols by shaking the corresponding alcohol in ether with β-acetobromoglucose and silver carbonate, and saponifying the resulting acetyl compound. The yield is considerably increased, if the acetobromoglucose is added in portions of 1 g. twice daily during the shaking, which is continued for several days.

Borneol. About three years ago, J. Aloy and V. Brustier[5]) found that when conducting borneol vapours over copper oxide, heated to 250 to 300°, camphor results, and that at from 420 to 430° a mixture of terpenes is formed. As they now communicate[6]), the dehydration likewise succeeds with other metallic oxides, which are not easily reducible, best with thorium oxide. They give particulars regarding the terpenes formed: the reduction with thorium oxide at 350° yields a liquid of a terpene-like odour and boiling at between 150 and 180°; d_{20° 0,8637; α_D + 1° 46'; n_{D20° 1,472. Three quarters of this product consist of pinene: b. p. 156 to 160°; d_{20° 0,871; n_{D20° 1,472. The authors did not prepare any derivatives of this pinene. The mixture of hydrocarbons, obtained from borneol with the aid of copper, had a similar composition.

In the *conversion of borneol into camphene,* a thorough change in the whole ring system takes place when the water is split off. As borneol may be considered to be a bicyclic pinacolin alcohol, it seems that the transposition, which takes place during the conversion into camphene, is closely connected with the rearrangement of atoms, observed when pinacolin alcohol is converted into tetramethylethylene. Already Wagner had, at the time, drawn a parallel between the formation of camphene from borneol and the conversion of pinacolin alcohol into tetramethylethylene. In order

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[1]) Comp. *Report* April **1909**, 125. — [2]) *Compt. rend.* **158** (1914), 1554. — [3]) Comp. *Report* October **1913**, 138. — [4]) *Biochem. Zeitschr.* **61** (1914), 1; *Chem. Zentralbl.* **1914**, I. 1887. — [5]) *Bull. Soc. chim.* IV. **9** (1911), 733; *Report* October **1911**, 141. — [6]) *Journ. de Pharm. et Chim.* VII. **10** (1914), 49.

to study more accurately the conversion of borneol into camphene, H. Meerwein[1]) examined pinacolin alcohols of monocyclic structure as to their behaviour in the process of splitting off water. He wanted to know above all whether the separation of water would also in these cases be accompanied by a change in the ring system. He investigated the course of the separation of water from the alcohols: 2,2-dimethyl *cyclo*hexanol-1, 3-*iso*propyl-1,1-methyl-α-oxethyl*cyclo*pentane and describes the preparation of 1,1-methylacetyl*cyclo*pentane.

It would lead us too far to enter any further into this work, and we must be satisfied with mentioning that the results of these laborious investigations form an excellent confirmation on an entirely new basis of Wagner's formula for camphene.

Regarding the β-glucoside of anisyl alcohol see page 79.

Aldehydes.

Reduction of aldehydes by means of yeast.

On page 128 of our previous *Report*, we discussed a paper by Steenbock and Neuberg on the formation of higher alcohols from aldehydes by means of yeast. In the same way, Neuberg and E. Welde[2]) reduced benzaldehyde and phenylacetaldehyde to the corresponding alcohols benzyl and phenylethyl alcohol by adding them to fermenting yeast. Benzaldehyde affords after a reaction of several days 22 to 27 p.c. of the theoretically possible quantity. As regards the reduction of phenylacetaldehyde, an acid reaction is best avoided by adding some calcium carbonate. In this manner 24 g. of phenylacetaldehyde yielded 8,5 g. phenylethyl alcohol.

As Neuberg and F. F. Nord[3]) proved, *n*-valeraldehyde can be easily reduced to *n*-amyl alcohol by means of fermenting yeast. This alcohol occurs in fusel oil. The authors determined its presence by oxidizing it into *n*-valeric acid, which was then identified by the properties of its calcium salt, as well as by its optical inactivity.

In a similar manner, Neuberg and Nord as well as E. Róna[4]) reduced *n*-capronaldehyde to *n*-hexyl alcohol (b. p. 156 to 157°), and cinnamaldehyde to cinnamyl alcohol (b. p. 248 to 252°).

An experiment to prepare synthetically α,β-hexenealdehyde has been mentioned on page 80 of this *Report*.

Phenylacetaldehyde. In order to prepare this aldehyde, P. Jehl[5]) proceeds as follows: 16 g. methyl cinnamate are dissolved in 20 g. of methyl alcohol, and 10 g. of bromine are added. The liquid congeals in the cold. Then a solution of 12 g. sodium hydroxide in 24 g. of water is added under shaking, the temperature not being allowed to exceed 40°. After two hours, the mixture is neutralized with sulphuric acid, when the flocculent precipitate dissolves and an oil separates. After dilution to 250 cc., 5,5 g. sodium carbonate are added, the phenylacetaldehyde is distilled with steam and the distillate extracted with ether. The yield amounts to 75 p.c. of what is calculated. If nitrocinnamic acid is treated in the same way, an aldehyde forms which smells like cinnamon. In order to explain this reaction it is supposed that at first dibromide

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[1]) *Liebig's Annalen* **405** (1914), 129. — [2]) *Biochem. Zeitschr.* **62** (1914), 477; *Chem. Zentralbl.* **1914**, II. 152. — [3]) *Biochem. Zeitschr.* **62** (1914), 482; *Chem. Zentralbl.* **1914**, II. 152. — [4]) *Biochem. Zeitschr.* **67** (1914), 137. — [5]) *Bull. Soc. ind. Mulhouse* **83** (1913), 805; *Journ. Soc. chem. Ind.* **33** (1914), 333.

forms from the ester and passes by hydrolysis into phenylglyceric ester. This ester transforms into the corresponding lactone and, by splitting off carbon dioxide, passes into phenylacetaldehyde.

E. Späth[1]) describes an interesting synthesis of phenylacetaldehyde and of some of its homologues. He found that the following reaction took place when alkyl-(aryl-) magnesium haloids acted on ethoxyacetal, which proved to be an easily accessible body: —

$$(OC_2H_5)\cdot CH_2\cdot CH(OC_2H_5)_2 + RMgX = C_2H_5OMgX + R\cdot CH(OC_2H_5)\cdot CH_2(OC_2H_5).$$

In addition, vinyl ethers form according to the following transposition: —

$$RCH(OC_2H_5)\cdot CH_2(OC_2H_5) + RMgX = C_2H_5OMgX + RH + RCH{:}CH(OC_2H_5).$$

When heated with dilute sulphuric acid, these ethers are saponified to aldehyde, passing through the stage of the unstable vinyl alcohol.

In this way, the synthesis of aldehydes of the formula $RCH_2\cdot CHO$ is given, and even most sensitive aldehydes may thus be prepared.

The substituted phenylacetaldehydes are bodies of agreeable odour; they are highly sensitive towards acids and alkalis and congeal on long storage, forming glassy substances.

The phenylethylaldehyde, obtained by Späth through the action of magnesium phenyl bromide or iodide on ethoxyacetal and saponification of the resulting mixture, boiled between 84 and 86° (10 mm.) and showed all the properties of this body.

From magnesium, *o*-iodotoluene and ethoxyacetal, *o*-methylphenylacetaldehyde was obtained, a colourless liquid of agreeable smell, boiling at 92° (10 mm.). *m*-Methylphenylacetaldehyde (b. p. 94° at 10 mm.) smells a little fainter than the *o*-combination. *p*-Methylphenylacetaldehyde boils at 96° (10 mm.). *m-p*-Dimethylphenylacetaldehyde boils between 112 and 114° (10 mm.), and *o-p*-dimethylphenylacetaldehyde, at from 106 to 108° (10 mm.). *o*- and *p*-Methylphenylacetaldehydes were already known.

Some years ago, F. W. Semmler and later on A. Wohl and R. Maag[2]) have studied the action of acetic anhydride on phenylacetaldehyde. Further particulars on the subject are found in an article now published by E. Späth[3]), in which he reports, besides, regarding the action of acetic anhydride on *iso*butyraldehyde and cinnamaldehyde.

It is a well known fact that phenylacetaldehyde is much inclined to polymerize, and that it is difficult, in consequence, to preserve it unaltered. This phenomenon has been carefully studied by H. Stobbe and A. Lippold[4]). In order to purify the aldehyde, it was distilled from a flask, which permitted of determining the temperature of the boiling liquid (on thermometer A), as well as that of the vapour passing over (on thermometer B)[5]). The main portion of the preparation passed over as almost pure phenylacetaldehyde. This is the period of distillation of the monomeric aldehyde. Thermometer A oscillated at first between 105 and 111° at 18 mm. and slowly rose on further heating from 112 to 160°, whereas thermometer B always showed 88° at 18 mm. The distillate which passed over last was pure phenylacetaldehyde, which had formed by decomposition from the polymeric aldehydes present in the preparation.

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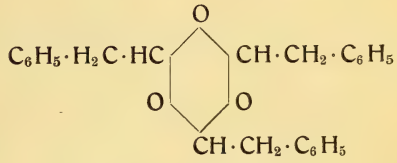
[1]) *Monatsh. f. Chem.* **36** (1915), 1. See also *ibidem* **35** (1914), 332. — [2]) *Berl. Berichte* **42** (1909), 584; **43** (1910), 3291; *Report* April **1909**, 128. — [3]) *Monatsh. f. Chem.* **36** (1915), 29. — [4]) *Journ. f. prakt. Chem.* II. **90** (1914), 277. — [5]) Stobbe and Reuss, *Liebigs Annalen* **391** (1912), 154.

After the monomeric phenylacetaldehyde had been rectified once more, it boiled at 88° (18 mm.) and the $n_{D20°}$ was 1,52204. The combustion and the determination of the molecular weight in boiling chloroform afforded values which corresponded to the formula C_8H_8O. On continuing the distillation after the monomeric phenylacetaldehyde had been obtained, fractions boiling from 88 to 97° and from 97 to 210° (18 mm.) were collected, which, as the determination of their molecular weights showed, contained a polymeride in addition to monomeric phenylacetaldehyde.

Various experiments were then made with regard to the polymerization of phenylacetaldehyde. In the presence of 23 p.c. sulphuric acid, phenylacetaldehyde, after several days' standing, deposited odourless, colourless crystals melting at 155 to 156°, for which the formula $(C_8H_8O)_3$ was ascertained by combustion and determination of the molecular weight, so that we have here to deal with a trimeric phenylacetaldehyde. It is easily soluble in benzene, chloroform, and acetone, sparingly soluble in alcohol, ether and glacial acetic acid, and almost insoluble in water. 2,7 p.c. of trimeric phenylacetaldehyde dissolve in the monomeric one. As contrasted with the monomeride, the trimeride is indifferent to ammoniacal silver solution; it does not add any sodium disulphite, does not afford an oxime, remains colourless in the presence of alcoholic potash and does not give any reaction with magenta and sulphurous acid. It has therefore no properties of the aldehydes. It is an analogue of paraldehyde and must therefore be designated a triphenylparaldehyde. It distils unaltered in the vacuum of the cathode rays and is, at 13 mm. partly, at atmospherical pressure completely, depolymerized to monomeric aldehyde.



Triphenylparaldehyde.

With concentrated sulphuric acid, at room temperature as well as at —80°, phenylacetaldehyde resinified.

In the presence of 23 p.c. hydrochloric acid, the aldehyde became thick at first, and after about two days solidified, forming an amorphous, odourless polymeride, which no longer showed any properties of an aldehyde.

When introducing dry hydrogen chloride into the aldehyde, it congealed to a viscid, sticky mass, which was not further investigated.

Phenylacetaldehyde remained almost unchanged with anhydrous formic acid, even after two days' standing. Glacial acetic acid and alcoholic solution of picric acid transformed it into a faintly yellow liquid.

In the presence of 10 p.c. aqueous potash lye, a solid, odourless resin formed, a dimeride of phenylacetaldehyde. It is not volatile in an unaltered state, not even in an absolute vacuum, and far more easily depolymerizable than triphenylparaldehyde. It may therefore be called diphenylmetacetaldehyde in analogy with metaldehyde. The same body results through the action of piperidine on phenylacetaldehyde.

In the dark and in ultraviolet light, phenylacetaldehyde polymerized without the addition of any catalysts at 21° to a thick oil, which was colourless and transparent, but not yet uniform. It contained monomeric phenylacetaldehyde and a viscid mass, which no longer gave the reaction with magenta and sulphurous acid, but on heating was split into the monomeric aldehyde. We have here to deal perhaps with a pentameride, $(C_8H_8O)_5$. Whereas the polymerization continues steadily in the dark, it apparently comes to a standstill on exposure to short-waved light, to go on all the quicker during the following dark period. There is therefore a photo-chemical after-effect. The stoppage during exposure may be explained by a state of equilibrium

between the spontaneous reaction in the dark (polymerization) and the photochemical reaction (depolymerization): $n C_8H_8O \underset{\text{light}}{\overset{\text{dark}}{\rightleftharpoons}} (C_8H_8O)n$. In order to study this polymerization process more closely, the authors determined the index of refraction, which shows higher values as the polymerization proceeds. On heating freshly prepared phenylacetaldehyde under pressure for some time, finally an odourless, opaque, viscid mass results, which does not show Caro's reaction and is therefore most likely identical with the pentameric product described above. On further heating, it depolymerizes into monomeric phenylacetaldehyde.

Phenylacetaldehyde likewise polymerizes in daylight, without the addition of any catalysts. Freshly distilled phenylacetaldehyde was preserved during a fortnight, at room temperature and in the dark, in an ordinary glass vessel and daily exposed to diffuse daylight for from 5 to 10 minutes, in order to measure the refraction. The substance remained liquid and colourless up to the 12th day, the index of refraction increasing steadily. On the 14th day, crystals of triphenylparaldehyde had formed. This likewise resulted after a long exposure to diffuse, long-waved daylight. Consequently polymerization of phenylacetaldehyde in the absence of catalysts leads to two different bodies, the quantities of which depend upon the intensity and the length of the light waves.

Stobbe and Lippold were able to confirm that moist phenylacetaldehyde is more stable than the dry substance, an observation which had been made *in praxi*. In the dark as well as when exposed to the light, moist aldehyde polymerizes more slowly than the dry one. Water therefore acts as a negative catalyst.

Benzylidene crotonaldehyde. Benzylidene crotonaldehyde (cinnamylidene acetaldehyde), as obtained in the manufacture of cinnamaldehyde, has been investigated by G. Engelberg[1]). He prepared it by condensing cinnamaldehyde and acetaldehyde and likewise examined a preparation supplied by our firm. The pure, recently distilled aldehyde is a pale yellow, refractive liquid, which soon becomes brown, when exposed to the air. If kept under water, it remains unaltered for a fairly long time. Its odour reminds one somewhat of cinnamaldehyde, and its taste is extremely burning; b. p. 176 to 178° (12 mm.). The aldehyde exists too in a beautifully crystallized modification of a rather unstable nature, which can be obtained by distillation *in vacuo* and treating the solid deposit in a centrifugal machine. Sol. p. 35°; m. p. 38,5°; $d_{19°}$ 1,16.

The sodium bisulphite compound cannot very well be used for separating benzylidene crotonaldehyde. It is difficult to purify it, and it decomposes easily. The phenylhydrazone forms beautiful, light yellow crystals melting at 177°, the semicarbazone melts at 229°. With hydrazine sulphate and sodium acetate, benzylidene crotonaldehyde forms an azine melting at 207°. The oxidation of benzylidene crotonaldehyde with ammoniacal silver solution leads to cinnamenylacrylic acid (m. p. 165°). Benzylidene crotonaldehyde cyanohydrine (m. p. 97°) was not saponifiable to the expected cinnamylidene-α-hydroxypropionic acid, but when being boiled with dilute hydrochloric acid it affords the transposition product of said acid, *i. e.* the isomeric benzallaevulic acid (m. p. 123°). By condensation of benzylidene crotonaldehyde with hippuric acid, a mixture of azlactones of benzylidene crotonaldehyde is formed, from which an azlactone melting at 203° and another melting at 162° could be isolated; this latter

[1]) *Über Benzylidencrotonaldehyd und einige seiner Kondensationsprodukte.* (On benzylidene crotonaldehyde and some of its condensation products.) Inaug.-Dissert., Berlin 1914.

is perhaps a mixture still. With malonic acid, benzylidene crotonaldehyde affords benzalcrotonylidene malonic acid, which seems to occur in different variable modifications. After condensation with pyrouvic acid, benzylidene crotonaldehyde yields benzalcrotonylidene pyroracemic acid, the phenylhydrazone of which melts at 175°. Condensation of benzylidene crotonaldehyde with acetaldehyde furnishes cinnamylidene crotonaldehyde, a reddish yellow, odourless body, which melts at 98°. The phenylhydrazone of cinnamylidene crotonaldehyde decomposes between 182 to 183°; the semicarbazone, at 238°.

$C_6H_5 \cdot CH:CH \cdot CHO$
Cinnamaldehyde.

$C_6H_5 \cdot CH:CH \cdot CH:CH \cdot CHO$
Benzylidene crotonaldehyde.

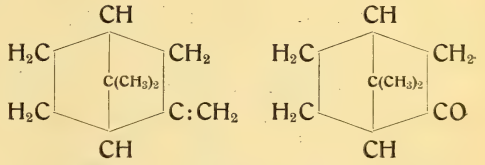
$C_6H_5 \cdot CH:CH \cdot CH:CH \cdot CH:CH \cdot CHO$
Cinnamylidene crotonaldehyde.

Ketones.

Fenchocamphorone. We reported at the time [1]) on the total synthesis of fenchocamphorone, carried out by G. Komppa, as per a short note in the "Original Communications, 8th Congress of Applied Chemistry, 1912, Vol. 25, p. 395". Komppa has now published details of this synthesis, as well as on the oxidation of the ketone with Caro's acid, in the *Berliner Berichte* [2]). By treating *D-d*-fenchocamphorone from *D-l*-fenchene with Caro's acid, a crude lactone was obtained, which was converted into bromo*apo*camphoric acid by means of hydrobromic acid and glacial acetic acid. After treatment with sodium carbonate, bromo*apo*campholic acid afforded *apo*campholide (m. p. 164°), which was identical [3]) with the *apo*campholide prepared by total synthesis from camphoric acid anhydride. Through this reaction the constitution of fenchocamphorone has been determined.

An identical *D-d*-fenchocamphorone is obtained according to Komppa and S. V. Hintikka [4]) from *D-l*-fenchene (prepared from fenchylamine as indicated by Wallach) on treatment with ozone in glacial acetic acid with 16 p.c. unwashed ozone. On decomposing the ozonide on a water-bath, a ketone was formed which, after recovery from the semicarbazone, melted between 109 and 110°. *D-l*-fenchene, derived from *l*-fenchyl alcohol by way of fenchyl chloride, yielded on ozonisation an aldehydelike body in addition to fenchocamphorone. The same reaction products resulted from *D-d*-fenchene. Besides, from either fenchene an acid formed, which melted at 70 to 71° but has not yet been further examined.

The results obtained in the ozonisation process confirm the formula presumed by Wallach for fenchene: —



Fenchene. ⟶ Fenchocamphorone.

Santenone. E. Rimini [5]) continued his investigations of santenone [6]). He exposed synthetic santenone in aqueous-alcoholic solution to the light from the middle of March to the middle of November. The resulting liquid gave the reaction with acetaldehyde and when being poured into water, separated an oil which chiefly consisted of unaltered santenone. On treating the reaction material with benzenesulphohydroxamic acid, a hydroxamic acid, $C_9H_{15}O_2N$ (m. p. 144 to 145°), was obtained, which after addition

[1]) Comp. *Report* October **1913**, 147. — [2]) *Berl. Berichte* **47** (1914), 933. — [3]) *Ibidem* **44** (1911), 1539. — [4]) *Ibidem* **47** (1914), 936. — [5]) *R. I. Lombardo di Scienze e Lettere; Estr. dei Rend.* **47** (1914), 110 (kindly sent us by the author); *Chem. Zentralbl.* **1914**, I. 1426. — [6]) Comp. *Report* April **1912**, 185; April **1914**, 138.

of sulphuric acid yielded an acid $C_9H_{14}O_2$ (probably a mixture of both π-norcampholenic acids) and a neutral compound, the lactone of oxydihydro-π-norcampholenic acid. Besides, during the exposure to the light an aldehyde had formed, which is characterized by a semicarbazone melting from 156 to 158°. An analogous investigation of camphor was carried out at the time by Ciamician and Silber[1]).

A. Kötz and E. Lemien[2]) report on the synthesis of terpene ketones, $C_{10}H_{16}O$, from ketones, $C_9H_{14}O$. They converted sabina ketone into hydroxymethylene sabina ketone (m. p. 51 to 52°) according to Claisen's[3]) method and reduced it, following the indications of Skita, with hydrogen and palladium chloride, to methyl sabina ketone, $C_{10}H_{16}O$, an intensely and agreeably smelling liquid, boiling at 221°. In the same way nopinone yielded over hydroxymethylenenopinone (m. p. 71 to 72°) methylnopinone, $C_{10}H_{16}O$, which smells considerably stronger than nopinone. B. p. 215 to 216°; semicarbazone, m. p. 179 to 180°. The authors indicate a second way to prepare methylnopinone. From nopinone and oxalic ester, by means of sodium ethylate, they arrived at nopinone oxalate (b. p. 158 to 160° at 17 mm.), which was transformed into nopinone carboxylate after several days' heating on a sand-bath. When heating sodium nopinone oxalate with a great excess of methyl iodide and under addition of alcohol, a slight reaction took place in the course of several days. On saponification a little methylnopinone was formed in addition to a lot of nopinone.

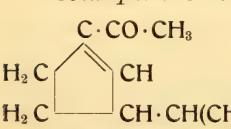
As to polymorphism of camphor see page 72.

Re rotary movements of camphor floating on water see page 73.

Epicamphor. Analogous to the synthesis of *l*-epicamphor[4]), R. Furness and W. H. Perkin[5]) have obtained *d*- and *d,l*-epicamphor. With the aid of sodium amide and carbonic acid, they converted *l*-camphor into *l*-camphorcarboxylic acid (m. p. 125 to 127°), which on electrolytical reduction yielded a mixture of *l*-borneolcarboxylic acids, from which under the action of acetyl chloride and subsequent distillation *l*-bornylene-3-carboxylic acid (m. p. 110 to 112°) resulted. The ester of this acid was converted into *l*-bornylene-3-hydroxamic acid (m. p. 135 to 136°), from which *d*-camphor resulted: m. p. 182°, $[\alpha]_D$ —98,9°; semicarbazone m. p. 237 to 238°; oxime m. p. 103°. *d,l*-epicamphor was prepared from its components as well as from *d,l*-bornylene-3-carboxylic acid. It melts at 180°; the oxime, between 98 and 100°.

Chlorocamphor. By heating α-chlorocamphor with sodium ethylate according to Kipping's[6]) method, T. M. Lowry and V. Steele[7]) obtained stereoisomeric α'-chlorocamphor, m. p. 117°; $[\alpha]_D$ + (?) 41,4° (5 g. on 100 cc. of alcohol). α-chlorocamphor showed in similar dilution $[\alpha]_D$ 97,0° (+ ?).

Iso*camphor.* In the course of his investigations of the terpenones of the camphor series, E. Rimini[7]) observed that, on reduction with colloidal palladium, *iso*camphor forms dihydro*iso*camphor. On oxidation of *iso*camphor, acetone, succinic acid and α-ketoglutaric acid are formed. Rimini ascribes to *iso*camphor the formula which Wallach had already declared probable[8]).



*Iso*camphor.

[1]) *Berl. Berichte* **43** (1910), 1340; *Report* October **1910**, 167. — [2]) *Journ. f. prakt. Chem.* II. **90** (1914), 314. — [3]) A. Kötz u. E. Schaeffer, *ibidem* II. 88 (1913), 605; *Report* April **1914**, 126. — [4]) Comp. *Report* April **1914**, 140. — [5]) *Journ. chem. Soc.* **105** (1914), 2024; *Chem. Zentralbl.* **1914**, II. 1315. — [6]) *Proceed. chem. Soc.* **21** (1905), 125. — [7]) *Ibidem* **30** (1914), 201. — [8]) *Rend. della Soc. Chim. Ital.* **1914**, 27 (the author kindly sent us a reprint); *Chem. Zentralbl.* **1914**, I. 1653. — [9]) *Liebigs Annalen* **392** (1912), 69; *Report* October **1912**, 160.

Homologues of camphor and borneol.

A few years ago, we discussed a paper by Haller and Bauer[1]) on dimethylcamphor and dimethylborneol and are now in a position to report on the preparation of some other derivatives of camphor and of borneol. A. Haller and J. Louvrier[2]) heated in a dry flask 152 g. of dry camphor with 39 g. of sodium amide[3]) and 500 g. of benzene free from thiophene. After the evolution of ammonia had lessened, 155 g. of ethyl iodide were added little by little, diluted with an equal quantity of benzene. The reaction, which was violent at the beginning, slackened down very soon, so that at the end it was necessary to heat for a few hours. In this way 45 to 50 p.c. of the theoretically possible quantity of monoethylcamphor were obtained, a body which had been prepared before by Brühl[4]) in a different manner. The reduction of ethylcamphor with sodium and alcohol led to ethylborneol (ethylcamphol). The author obtained in a similar way several other alkyl derivatives of camphor and borneol, the properties of which are given below in the form of tables: —

Alkylcamphors and alkylborneols.

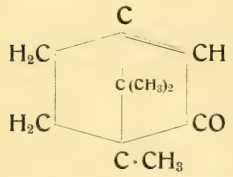
	b. p.	$d\frac{0°}{0°}$	α_D in alcohol about	
Camphor derivatives				
Monoethylcamphor . .	108° (14 mm.)	0,927	+ 45°	Camphorlike smelling liquid. Oxime, m. p. 93°.
Diethylcamphor	132 to 133° (14 mm.)	0,969	+ 91°	Liquid, does not smell any more like camphor.
Methylethylcamphor .	112 to 114° (11 mm.)	—	+ 99° 30′	Liquid.
Propylcamphor[5]) . . .	116° (11 mm.)	0,942	+ 60° 40′	Liquid. Oxime, m. p. 79°.
Dipropylcamphor . . .	157° (14 mm.)	—	+ 53° 50′	Liquid.
Benzylcamphor[6]) . . .	—	—	+ 147° 40′	m. p. 51°.
Dibenzylcamphor . . .	255° (12 mm.)	—	+ 103° 10′	m. p. 103°.
Ethylbenzylcamphor .	193° (11 mm.)	—	+ 91°	Viscid.
Borneol derivatives				
Ethylborneol	110° (14 mm.)	—	+ 37°	Borneollike smelling liquid. Phenylurethane, m. p. 47°.
Diethylborneol	134° (12 mm.)	—	+ 51°	Viscid, smells like borneol. Phenylurethane, m. p. 106°.
Methylethylborneol . .	120° (130 mm.)[7])	—	+ 38° 40′	Viscid.
Propylborneol[5])	110° (11 mm.)	—	—	m. p. 59°.
Dibenzylborneol . . .	—	—	— 15°	m. p. 84°. Phenylurethane, m. p. 82°.

Cyclo*camphanone*. By the action of nitrous acid on aminocamphor, a ketone is formed, which Angeli[8]) many years ago called camphenone, as he supposed that

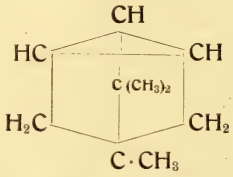
[1]) *Compt. rend.* **148** (1909), 1643; *Report* October **1909**, 199. — [2]) *Compt. rend.* **158** (1914), 754. — [3]) Comp. *Report* October **1913**, 146. — [4]) *Berl. Berichte* **24** (1891), 3382. — [5]) Haller and Minguin had previously prepared it. *Compt. rend.* **142** (1906), 1309; *Report* October **1906**, 134. — [6]) Haller and March, *Compt. rend.* **142** (1906), 316; *Report* April **1906**, 101. — [7]) 13 mm.? — [8]) *Gazz. chim. ital.* **24** (1894), II. 44, 317; *Berl. Berichte.* **27** (1894), 590, 892 (Abstracts).

there was an ethylenic linking in it, like in camphor (I). According to Holz[1]), however, this supposition does not agree with the facts, as there would be a ethylenic linking to a tertiary hydrocarbon, which is common to two rings, and this is impossible for stereochemical reasons. The ketone rather contains a trimethylene ring. Holz replaced the oxygen in Angeli's camphenone by hydrogen, following the method of Kishner[2]) and Wolff[3]) and thus obtained an optically inactive hydrocarbon $C_{10}H_{16}$ (m. p. 117 to 118°), which distinguishes itself from camphane in that it contains a new ring linking in the molecule and two atoms of hydrogen less. Holz calls this hydrocarbon *cyclo*camphane (II) and the corresponding ketone (Angeli's camphenone), *cyclo*camphanone (III). After reduction with sodium and alcohol, *cyclo*camphanone affords a new borneol, *cyclo*camphanol, $C_{10}H_{16}O$, melting between 174 and 176°. It resulted from the difference between the calculated and the established molecular refraction that there is no double linking in the molecule, but an exaltation of about 0,7 indicated the presence of a tricyclic ring.

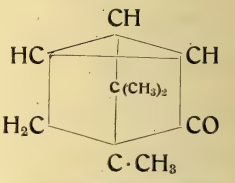
By splitting off water from the oxime of *cyclo*camphanone, the nitrile of *cyclo*campholenic acid is obtained, which can be saponified with alcoholic potash lye to *cyclo*campholenic acid, $C_{10}H_{14}O_2$ (IV), which through oxidation passes into *cyclo-iso*camphoronic acid, $C_9H_{12}O_6$ (V), melting between 228 and 230°. The formation of the last-named acid conclusively proves the constitution of *cyclo*camphanone.



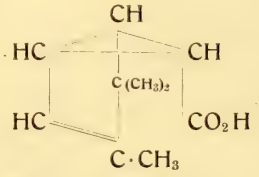
(I) Angeli's formula for camphenone.



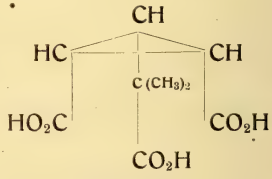
(II) *Cyclo*camphane.



(III) *Cyclo*camphanone.



(IV) *Cyclo*campholenic acid.



(V) *Cycloiso*camphoronic acid.

Thujone. As is known, by isomerization of thujone, *iso*thujone is obtained. This yields on reduction thujamenthol, which can easily be oxidized to thujamenthone. According to M. Godchot[4]), thujamenthone can be prepared in a simpler way by reducing thujone with hydrogen and nickel at from 175 to 180°. The thujone employed by him boiled at 199 to 201°; $d_{15°}$ 0,9190; α_D — 29,54°; $n_{D17°}$ 1,4546. The reduction product, thujamenthone, boiled from 207 to 209°; $d_{20°}$ 0,8844; $n_{D20°}$ 1,4526. The semicarbazone melted at 178 to 179°; the oxime, at 95°. *Iso*thujone likewise affords thujamenthone on reduction with hydrogen and nickel.

Wallach[5]) too reduced *iso*thujone at the time and obtained thujamenthone, whereas thujone remained indifferent to the palladium atom charged with hydrogen.

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[1]) *Zeitschr. f. angew. Chem.* **27** (1914), I. 347. — [2]) Comp. *Report* April **1912**, 195. — [3]) *Liebigs Annalen* **394** (1912), 94; *Report* April **1913**, 139. — [4]) *Compt. rend.* **158** (1914), 1807. — [5]) *Liebigs Annalen* **381** (1911), 85; *Report* April **1911**, 165.

C. Agostinelli[1]) heated an alcoholic solution of thujone with ammonium hydrogen sulphide for 24 hours in a sealed tube up to 150° and obtained a brown, somewhat viscid mass, from which *iso*thujone (as oxime or semicarbazone, respectively) and thio*iso*thujone, $C_{10}H_{16}S$, could be isolated. The isomerization of thujone is due most likely to the hydrogen sulphide, as it likewise occurs on heating with ammonium hydrogen sulphide to 60°. From *iso*thujone and ammonium hydrogen sulphide also only impure thio*iso*thujone formed.

There are, in consequence, two phases of action of ammonium hydrogen sulphide on thujone: in the first the isomerization to *iso*thujone takes place; in the second, this is converted into a mixture of polysulphides, in which only the presence of thio-*iso*thujone could be proved.

Carone. By heating carone with ammonium hydrogen sulphide under pressure, C. Agostinelli[2]) obtained a mixture, which was separated into fractions by steam distillation. From the volatile part, a body of the formula $(C_{10}H_{17})_2S_2$ was isolated; m. p. 238 to 242°. The residue which remained after distillation with steam, a dark red oil, decomposed between 80 and 90°. The contents of sulphur pointed to a pentasulphide, $C_{40}H_{68}S_5$.

Carvone. Some years back, G. Ciamician and P. Silber[3]) obtained on exposure of carvone to the light an isomeric body (m. p. 100°; b. p. 206,5°), which showed great similarity with camphor. E. Sernagiotto[4]) investigated this compound more closely and suggests for it the name of carvonecamphor. The oxidation with potassium permanganate led to a dibasic acid, $C_{10}H_{14}O_4$, melting at 174°, and a ketonic acid, $C_9H_{12}O_3$, melting at 100°, which latter can also be obtained from the dibasic acid by means of potassium permanganate. The ketonic acid is characterized by a phenylhydrazone melting at 176° and an oxime melting at 167°. When being treated with alcoholic sulphuric acid, carvonecamphor yields *iso*carvonecamphor, an oil boiling between 222 and 224°. The oxime melts at 167°; the semicarbazone, at 209°. Through reduction with palladium and hydrogen, dihydro*iso*carvonecamphor results, an oil boiling at 224°.

If carvonecamphor is reduced with sodium and alcohol, carvoneborneol forms (m. p. 135°; b. p. 214°), which by oxidation with Beckmann's chromic acid mixture may be reconverted into carvonecamphor, which under the action of the oxidizing mixture partly isomerizes to *iso*carvonecamphor.

H. Rupe and W. Tomi[5]) report on some high molecular, optically active hydrocarbons and ketones derived from carvone. From magnesium phenyl bromide and carvone, they obtained 2-phenyl-*p*-menthadien-6,8(9)-ol-2 (2-phenylcarveol), a liquid boiling at 164,5 to 165,5° (10 mm.). In order to prepare 2-phenyl-*p*-menthatriene-2,6,8(9), the authors added the ethereal solution of the addition product of magnesium phenyl bromide and carvone in drops and under cooling to 30 p.c. sulphuric acid. The resulting hydrocarbon boiled at 149 to 150° (10 mm.); $\alpha_{D15°}$ 65,32°. Klages[6]) observed at the time the boiling point of 159 to 160° for phenylcarveol (12 mm.) and + 110,2° as highest optical rotation for phenylmenthatriene. It is therefore doubtful whether we

[1]) *Gazz. chim. ital.* **44** (1914), II. 111; *Chem. Zentralbl.* **1914**, II. 1438. — [2]) *Gazz. chim. ital.* **44** (1914), II. 111; *Chem. Zentralbl.* **1914**, II. 1439. — [3]) *Berl. Berichte* **41** (1908), 1931; *Report* November **1908**, 159. — [4]) *Atti R. Accad. dei Lincei, Roma* (5) **23** (1914), I. 70; *Chem. Zentralbl.* **1914**, II. 1398. — [5]) *Berl. Berichte* **47** (1914), 3064. — [6]) *Berl. Berichte* **39** (1906), 2306; *Report* October **1906**, 131.

have here to deal with the same bodies. The 2-phenyl-*p*-cymene mentioned already by Klages, was obtained by boiling phenylmenthatriene with sulphuric and glacial acetic acids. The action of magnesium benzyl chloride on carvone produces three bodies, the principal one being a ketone, 6-benzyl-*p*-menthen-8(9)-one-2 (6-benzyldihydrocarvone); m. p. 73°; b. p. 181 to 184° (11 mm.); oxime, m. p. 140 to 141°. This ketone did not yield any semicarbazone with semicarbazide, but an addition product, $C_{18}H_{27}N_3O_2$. Besides, there forms from magnesium benzyl chloride and carvone a hydrocarbon, $C_{17}H_{20}$, (b. p. 162 to 166° at 10 mm.), and another of the same empirical composition, but which boils between 169 and 173° (10 mm.). When the mixture of these hydrocarbons was treated with sulphuric and glacial acetic acids, 2-benzyl-*p*-cymene resulted (b. p. 165 to 167° at 12 mm.). *α*-methylbenzyl magnesium bromide reacts with carvone under the formation of an optically inactive hydrocarbon, $C_{18}H_{20}$, melting at 127°.

Through the action of Grignard's salts on benzyldihydrocarvone, secondary alcohols are obtained, from which potassium pyrosulphate splits off water with formation of hydrocarbons. In this way magnesium methyl iodide and 6-benzyl-*p*-menthen-8(9)-on-2 afforded 6-benzyl-2-methyl-*p*-menthen-8(9)-ol-2, boiling at 188 to 190° (10 mm.), from which 6-benzyl-2-methyl-*p*-menthadiene-2,8(9) (b. p. 169 to 172° at 11 mm.) was prepared by dehydration. The authors further describe the corresponding propyl, phenyl and benzyl compounds.

By treating benzyldihydrocarvone with phosphorus pentachloride and reducing the chloride formed with sodium and alcohol, one arrives at a diolefinic hydrocarbon $C_{17}H_{22}$, presumably 6-benzyl-*p*-menthadiene-2,8(9) (b. p. 167 to 169° at 14 mm.). The action of ozone on benzyldihydrocarvone (6-benzyl-*p*-menthen-8(9)-on-2) produces an ozonide, which has not been investigated more closely so far, but which easily passes into a diketone melting at 78°, 1-methyl-6-benzyl-4-acetylcyclohexanone-2; dioxime, m. p. 195 to 196°. The same diketone forms, although less readily, when benzyldihydrocarvone is treated with chromic acid or potassium permanganate. When melting 6-benzyl-*p*-menthen-8(9)-on-2 with caustic potash, carvacrol was obtained.

A. Claus and W. Fahrion, as well as Schimmel & Co.[1]) indicate 210 to 211° as melting point for the combination of carvone with hydrogen sulphide, whereas according to A. Beyer[2]) (Copenhagen) it melts at 187°. Of late, E. Deussen[3]) occupied himself whit this combination and found that *d*- and *l*-carvone hydrogen sulphide really melt at 210 to 211°. The determination of the freezing points showed that the combinations behave like dimolecular bodies in benzene, but like monomolecular ones in glacial acetic acid. For a solution of about 6 p. c. in chloroform, the following values of specific rotation were found: $[\alpha]_{D18°} + 48{,}71°$ and $[\alpha]_{D22°} - 48{,}44°$. Inactive carvone hydrogen sulphide, however, melts at 189 to 190°. In order to purify the substance, it was precipitated from chloroform by means of ethyl acetate.

Deussen further describes some experiments to brominate carvoxime and benzoylcarvoxime. He added 3 atoms of bromine to *d*- and *l*-carvoxime dissolved in chloroform, cooling very strongly, and obtained a tribromide: m. p. 119 to 128°; $[\alpha]_{D19°} - 15{,}17°$ and $+ 14{,}87°$ in an about 6,7 p. c. solution in benzene. The inactive compound melted at 128°. In the same manner he prepared the tetrabromide of *d*- and *l*-carvoxime. The direction of the rotations ($[\alpha]_{D22°} - 10{,}70°$ and $[\alpha]_{D21.5°} + 11{,}09°$ in an about 8 p. c. solution in benzene) was opposed to that of the raw material. The inactive compound

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[1]) *Journ. f. prakt. Chem.* II. **39** (1889), 365; *Report* April **1898**, 47, foot note. — [2]) *Arch. der Pharm.* **221** (1883), 285. — [3]) *Journ. f. prakt. Chem.* II. **90** (1914), 318.

melted at 121,5°. The benzoylcarvoximes furnish dibromides melting at 140 to 141° ($[\alpha]_{D200}$ +5,66° and $[\alpha]_{D240}$ —5,11° in an about 2 p. c. solution in benzene); the inactive compound melts at 121°.

At an earlier opportunity, A. Hahn[1]) prepared *L*- and *R-d*-tetrabromocarvoxime-benzoyl esters. When repeating the experiment, Deussen succeeded in splitting the tetrabromo compound into two isomerides, *viz.*, *L-d*- or *R-l*-tetrabromo-*α*-benzoylcarvoxime-*a*, insoluble in alcohol and melting at 136 to 137°, and a *L-d*- or *R-l*-tetrabromo-*α*-benzoylcarvoxime-*b*, easily soluble in alcohol and melting at 119 to 120°. The inactive form of the *α*-compound melts at 145°; that of the *b*-compound, at 127 to 127,5°.

In an article published at the beginning of 1914, O. Wallach[2]) described the reduction of carvone and carvoxime by means of hydrogen and palladium. He obtained, according to the conditions under which the experiments were carried out, carvotanacetoxime or tetrahydrocarvoxime, in addition to carvacrylamine and tetrahydrocarvone. An electrolytical reduction of carvoxime in alkaline solution, undertaken by H. Rupe and K. Löffl[3]), yielded a fair quantity of pure dihydrocarvone, in addition to unaltered carvoxime. Presumably carvoxime is first reduced to dihydrocarvoxime, which is then saponified. The semicarbazone of the dihydrocarvone thus obtained melted between 189 and 191°. No other reduction product of dihydrocarvone could be traced.

Hexahydro-ψ-ionone. N. Ishizaka[4]) reports on the preparation of hexahydro-*ψ*-ionone and of some of its derivatives. He reduced geraniol according to Paal's method with palladium and hydrogen in methyl alcoholic solution to tetrahydrogeraniol, boiling at 212 to 213°. In this manner, the hydroxyl group remains unattacked, whereas on hydrogenation with platinum and hydrogen[5]) a mixture of dimethyloctane and dimethyloctanol results. By means of phosphorus tribromide, tetrahydrogeraniol was converted into tetrahydrogeraniol bromide (b. p. 104 to 105° at 14 mm.), which with ethyl sodioacetoacetate affords ethyl tetrahydrogeranylacetoacetate (b. p. 164 to 166° at 10 mm.). On prolonged standing with alcoholic potash lye the ester is converted into hexahydro-*ψ*-ionone. The ketone, recovered from the semicarbazone (m. p. 95 to 96°), boils at 119 to 120° (10 mm.) and has lost its aromatic character. The oxime of hexahydro-*ψ*-ionone boils at 159 to 160° (13 mm.).

Phenols and Phenol-ethers.

The ether-oxides of carvacrol. Following up former treatises on the preparation of mixed ethers of alcohols and phenols[7]), P. Sabatier and A. Mailhe[8]) report on the catalytic production of ether-oxides of carvacrol. In the presence of thorium oxide, the dehydration of carvacrol between 400 and 500° is rather complicated. Carbon monoxide and hydrocarbons are evolved and an oily mixture of carvacryl and dicarvacrylene oxides forms. If a mixture of carvacrol and methyl alcohol is passed over thorium oxide at 420 to 450°, in addition to carvacryl methyl ether, dicarvacryl oxide forms, $\begin{matrix}C_3H_7\\CH_3\end{matrix}\!\!>\!C_6H_3\cdot O\cdot C_6H_3\!<\!\begin{matrix}C_3H_7\\CH_3\end{matrix}$, a substance consisting of colourless prisms which melts at 109 to 110° and is soluble in most of the organic solvents. If the catalysis takes

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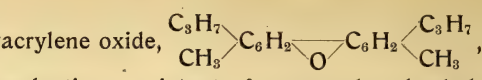
[1]) Comp. *Report* April **1910**, 177. — [2]) *Liebigs Annalen* **403** (1914), 73; *Report* April **1914**, 142. — [3]) *Berl. Berichte* **47** (1914), 2150. — [4]) *Berl. Berichte* **47** (1914), 2453. — [5]) Comp. R. Willstätter and E. Mayer, *ibidem* **41** (1908), 1475; *Report* November **1908**, 153. — W. Ipatiew, *Berl. Berichte* **45** (1912), 3218; *Report* April **1913**, 134. — [7]) *Compt. rend.* **151** (1910), 359, 492. — [8]) *Compt. rend.* **158** (1914), 608.

place at 480°, dicarvacrylene oxide,  , is formed besides. It melts at 150°. On conducting a mixture of carvacrol and ethyl alcohol over thorium oxide at a temperature of from 400 to 500°, in addition to small quantities of carvacryl ethyl ether, a body is obtained which is perhaps identical with the oily product resulting from carvacrol. An equimolecular mixture of carvacrol and phenol yields, in the presence of thorium oxide and at from 470 to 480°, phenyl carvacryl oxide (b. p. 296°) as well as dicarvacryl and dicarvacrylene oxides. A mixture of carvacrol and *p*-cresol, however, produces at from 440 to 450° *p*-tolyl carvacryl oxide (b. p. about 300°) and *p*-tolyl oxide. At 480°, the catalysis leads exclusively to a mixture of *p*-tolyl oxide and *di-p*-cresylene oxide.

Eugenol. In the same manner as former editions of the German pharmacopoeia did for clove oil as well as for eugenol, the *Pharmacopoea Austriaca* VIII takes into consideration an adulteration of eugenol with carbolic acid. It prescribes that 1 g. of the oil ought to be shaken with 20 g. of hot water and 1 drop of ferric chloride solution, added to the filtrate obtained after cooling. The liquid may at most temporarily colour greenish, but not blue.

Quite apart from the fact that one is here on the look-out for an adulteration which has most likely never occurred yet, the test is liable to lead to an erroneous conclusion, as according to our experience with our own preparations, a blue tint of the water may result even with pure eugenol and ferric chloride. Recently prepared as well as recently rectified eugenol of older date did not give the reaction immediately after the distillation, but already after one day's standing the water, with which the eugenol had been shaken, coloured blue on addition of ferric chloride. Preparations which had been stocked for some time gave bluish tints from the very beginning, which must lead the casual observer to the conclusion that carbolic acid is present. In consequence, Austrian pharmacists told us repeatedly that our eugenol had been rejected at the official revision, as on account of said test it had been looked upon as containing carbolic acid. As it goes without saying that we sell exclusively pure eugenol free from any admixtures, and as we convinced ourselves at the same time of the misleading result of the reaction in question, we feel compelled to mention the matter here and to urge its being abandoned. In any case it is evident that it does not fulfil the purpose for which it is meant, but on the contrary gives rise to erroneous estimations, so that it is impracticable as a criterion for eugenol and ought not therefore, to be found in any pharmacopoeia.

As with freshly distilled eugenol ferric chloride does not colour the water blue, the reaction depends most likely on oxidation processes, which take place during the storage of the oil.

R. F. Weinland and H. Neff[1]) succeeded in preparing compounds of eugenol and vanillin with iron in the form of a complex anion. They are obtained from alcoholic solution of ferric acetate, eugenol, vanillin and alcoholic lye in determined quantities. The phenols must be present in considerable excess, so that the alkalis cannot precipitate any ferric hydroxide out of the ferric acetate. This large excess of eugenol in the preparation of the potassium eugenol-ferrate leads to the co-separation of the potassium salt of eugenol. It is then removed by washing with alcohol. Sodium tetra-

[1]) *Arch. der Pharm.* **252** (1914), 600.

vanillin-ferrate, $[Fe(C_6H_3(CHO)(OCH_3)O)_4]Na + {}^1/_2H_2O$, forms an almost black powder, which under the microscope appears to be composed of tiny reddish violet needles. There are further described: potassium pentavanillin-ferrate, sodium tetraeugenol-ferrate, a compound of potassium tetraeugenol ferrate and eugenol and the potassium salt of tetraeugenolferric acid.

The ferric acid of methyl salicylate had previously been prepared[1]).

Several years ago, M. Otto and A. Verley[2]) found that *iso*eugenol can be converted into vanillin by oxidation with ozone. A German firm opposed at the time the grant of a patent for this process, alleging that it was impracticable. By order of the German Patent Office, O. N. Witt undertook the verification and, on account of his experiments, arrived at the conclusion that the French method did not lead to the indicated results. Nevertheless a French factory produced several kilos of vanillin daily by this process, Later on it was compelled, it is true, to stop the manufacture, as the ozonation did not work properly and did not pay either.

The investigations, continued through many years by C. Harries, have now led to a complete elucidation of the process chemically speaking, on which he reports together with R. Haarmann[3]). It has been found that the preparation of vanillin from *iso*eugenol affords a satisfactory yield only if ozone of low percentage is used. Witt[4]) employed from the very beginning a big apparatus for the production of concentrated ozone, as in the application for a patent much stress had been laid on the use of a highly concentrated ozone, which, according to the conception of those days, corresponded to air containing 3 p.c. ozone. As Harries remarks, in this way Witt could only arrive at resinous products when starting from *iso*eugenol. Harries and Haarmann succeeded best with a 1 p.c. ozone. In this manner they treated not only *iso*eugenol, but also some other phenols and phenolethers. They prepared 1 p. c. ozone by conducting 14 p.c. ozone first through 5 p.c. soda lye, then through concentrated sulphuric acid and finally through a tube 40 cm. long and containing phosphorus pentoxide, thus considerably reducing the contents of ozone. In hexane solution *iso*eugenol gave a rather unstable, normal ozonide. In another experiment, *iso*eugenol in glacial acetic acid was saturated with 1 p. c. ozone and the solution heated on a water-bath, when gases were evolved and acetaldehyde escaped. After the glacial acetic acid had been distilled off *in vacuo,* an oil remained, from which by repeated distillation 37,8 p.c. of the theoretically possible quantity of vanillin was obtained.

Oxygen alone can likewise oxidize *iso*eugenol to vanillin. For this purpose dry oxygen was introduced into a solution of *iso*eugenol in glacial acetic acid, when at least 12 p. c. of vanillin formed.

A much better yield of vanillin is obtained by reducing the ozonide. *Iso*eugenol in dry ethyl acetate was saturated with 1 p.c. ozone, the acetate distilled off *in vacuo,* the oily residue, *iso*eugenol ozonide, dissolved in ether and reduced by gradually adding zinc dust and glacial acetic acid under cooling. After the excess of zinc dust had been removed, the ethereal solution was shaken with precipitated calcium carbonate and water, the ether being then removed and evaporated. The residue yielded 71 p.c. of vanillin (m. p. 73°) on distillation *in vacuo.* The yield is not inconsiderably increased if the distillation is carried out under strongly reduced pressure at 0,3 to 0,5 mm.

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[1]) Weinland and A. Herz, *Liebigs Annalen* **400** (1913), 225. — [2]) *Annal. de Chim.* VII. **13** (1898), 120; *Chem. Zentralbl.* **1898**, I. 307. — A. Trillat, *Compt. rend.* **133** (1901), 822. — Otto and Verley, *D. R. P.* 97620; *Chem. Zentralbl.* **1898**, II. 693. — [3]) *Berl. Berichte* **48** (1915) 32. — [4]) *Ibidem* 231. See also C. Harries, *ibidem* 410.

In the fission of the ozonide of *iso*eugenyl acetate, only acetyl vanillic acid was obtained. It is remarkable that on ozonization *iso*eugenyl acetate takes up more oxygen than what corresponds to its normal degree of saturation.

Normal eugenol ozonide, described already by Riedl von Riedenstein[1]), explodes much more easily than *iso*eugenol ozonide. It was reduced with zinc dust and afforded a good yield of *homo*vanillin (b. p. 111 to 114° at 0,45 mm.), a body of vanilla odour. The *p*-nitrophenylhydrazone melts at 150°; the semicarbazone, at 173° and the oxime, at 115°. On being shaken with sodium disulphite solution, *homo*vanillin affords a sparingly soluble, white, powdery double compound which, however, has not a normal composition.

Eugenyl acetate forms, contrary to *iso*eugenyl acetate, a normal ozonide. On fission with glacial acetic acid, it yields aceto*homo*vanillic acid (m. p. 134°) and most likely acetyl*homo*vanillin too.

On fission of methyleugenol ozonide[2]) with glacial acetic acid, methylvanillin results, the *p*-nitrophenylhydrazone of which melts at 210°.

The reduction of methyleugenol ozonide can be carried out in the same way as that of eugenol or *iso*eugenol ozonides. Methyl*homo*vanillin is then formed, which is characterized by a *p*-nitrophenylhydrazone melting at 157° and a semicarbazone melting at 181°.

Safrole. We may here discuss a few derivatives of safrole and *iso*safrole out of a series described by R. P. Foulds and R. Robinson[3]). 6-Nitrosafrole is obtained by nitration of safrole dissolved in acetic acid; m. p. 25°. It is oxidized with potassium permanganate in acetone to 6-nitropiperonylacetic acid (m. p. 183°). The reduction of nitrosafrole with tin and hydrochloric acid leads to 6-aminosafrole (b. p. 168° at 15 mm.). Safroleazo-β-naphthol (m. p. 166 to 167°) results from safrolediazonium chloride and β-naphthol.

*Iso*safrole in chloroform yields with bromine in excess bromo*iso*safroledibromide with one bromine atom in the ring, whereas in carbon disulphide *iso*safroledibromide is formed in the normal way. On distillation under reduced pressure it decomposes into hydrogen bromide and bromo*iso*safrole. When bromo*iso*safrole is heated with methyl alcohol and potassium hydroxide, piperonylallylene is formed; m. p. 42 to 43°; b. p. 141°.

Iso*safrole.* It is known that there are two modifications of *iso*safrole, named α- and β-*iso*safrole[4]) and distinguished from one another only by their physical properties. M. Mayer[5]) purified β-*iso*safrole by way of the picrate (m. p. 75°). It boils at 250° and can be converted into two polymerides (m. p. 95 and 150°, respectively), described by us as well as by Puxeddu, Angeli and Mola[6]). Mayer examined the spectro-chemical behaviour of both polymerides in the ultraviolet region. Both showed a very constant absorption line in ultraviolet, beginning at 340 $\mu\mu$. The spectroscopical behaviour of either isomeride indicates that they have the same molecular structure.

Buchu camphor. G. Cusmano and P. Poccianti[7]) describe the conversion of dibromotetrahydrocarvone into buchu camphor. They prepared tetrahydrocarvone, following

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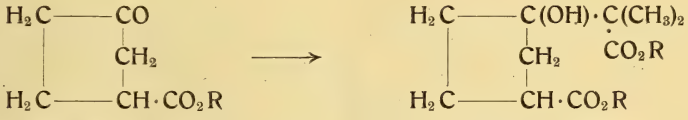
[1]) *Inaug.-Dissert.*, Kiel 1911. — [2]) Comp. R. Majima, *Berl. Berichte* **42** (1909), 3665. — [3]) *Journ. chem. Soc.* **105** (1914), 1963; *Chem. Zentralbl.* **1914**, II. 1188. — [4]) Comp. *Report* April **1910**, 186. — [5]) *Atti R. Accad. dei Lincei, Roma* (5) **23** (1914), 358; *Chem. Zentralbl.* **1914**, II. 475. — [6]) Comp. *Report* April **1905**, 18; October **1913**, 148. — [7]) *Atti R. Accad. dei Lincei, Roma* (5) **23**, I. (1914), 347; *Chem. Zentralbl.* **1914**, II. 481.

Vavon's[1]) indications, through catalytical reduction of carvone with hydrogen and platinum black. By adding bromine in drops to the chloroform solution of tetrahydrocarvone, dibromotetrahydrocarvone (m. p. 81°) is obtained. On being shaken with potash lye, it passes into buchu camphor, and this more quickly and more completely than dibromomenthone[2]).

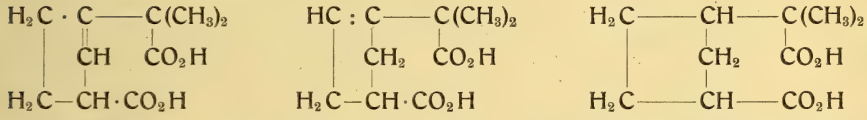
As regards the absorption spectrum of buchu camphor in the ultraviolet region see page 74.

Acids.

Camphenic acid. The constitution of camphenic acid (camphenecamphoric acid), an oxidation product of camphene, had not, so far, been established with certainty[3]). A little while ago, P. Lipp[4]) prepared synthetically *d,l-cis*-camphenic acid and recognized it to be a 1,3-carboxy*cyclo*pentane*iso*butyric acid, as Aschan had presumed already at



(I) ethyl 1,3-*cyclo*pentanone carboxylate. (II) 1,3-carbethoxy*cyclo*pentanol-*iso*butyrate.



(III) 1,3-carboxy*cyclo*pentene*iso*butyric acid. (IV) (V) 1,3-carboxy*cyclo*pentane*iso*butyric acid (camphenic acid) (Aschan's formula).

the time. He started from ethyl 1,3-*cyclo*pentanone carboxylate (I), which may be prepared even though with some difficulty according to the method described by Kay and Perkin as well as by Haworth and Perkin[5]). With zinc and α-bromo*iso*butyrate, this ester affords ethyl 1,3-carbethoxy*cyclo*pentanolbutyrate (II). On being treated with potassium pyrosulphate at 170 to 180°, it yields, in addition to the expected ethyl 1,3-carbethoxy*cyclo*pentene*iso*butyrate, an unsaturated ester acid, which presumably contains tertiary carboxyl still in the form of an ester. Both furnish on saponification with alcoholic potash 1,3-carboxy*cyclo*pentene*iso*butyric acid, for which two formulas are possible (III and IV). The hydrogenation of this acid according to Fokin-Willstätter's method leads to 1,3-carboxy*cyclo*pentane*iso*butyric acid, which proved to be identical with *d,l-cis*-camphenic acid (V). It melts at 135 to 137°, and there is no lowering of the melting point when it is mixed with pure *d,l-cis*-camphenic acid.

The paper published by Lipp agrees in many respects with an investigation of the structure of camphene, undertaken by W. N. Haworth and A. T. King[6]), following up previous examinations[7]), but the results of which they had not yet published. They now refrain from reporting fully on their work, describing only some syntheses which Lipp had not mentioned. This refers to the condensation of ethyl *as*-dimethyl

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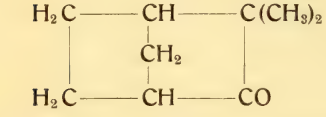
[1]) Comp. *Report* October **1911**, 150. — [2]) Comp. *Report* April **1914**, 139. — [3]) Comp. *Report* April **1911**, 188; October **1911**, 132; October **1913**, 131. — [4]) *Berl. Berichte* **47** (1914), 871. — [5]) Comp. *Report* October **1908**, 164. — [6]) *Journ. chem. Soc.* **105** (1914), 1342. — [7]) Comp. *Report* April **1913**, 135.

succinate with ethyl oxalate, with formation of ethyl oxalyl-*as*-dimethyl succinate and other bodies; the condensation of ethylmonomethyl succinate with ethyl oxalate, when ethyloxalylmonomethyl succinate results; the preparation of ethyl α,α-dimethylbutane-γ-one-α,δ,δ-tricarboxylate; the synthesis of ethyl α,α-dimethylbutane-γ-ol-$\alpha,\gamma,\delta,\delta$-tetracarboxylate and the corresponding lactone, as well as the production of butane-α,β,δ-tricarboxylic acid.

Camphenic acid is to be considered, as O. Aschan[1]) says, a secondary oxidation product of camphene and forms owing to a transposition of camphenylic acid. By heating with concentrated potash lye he succeeded in immediately converting camphenylic acid into camphenic acid. For this purpose, sodium camphenylate, obtained as a by-product of the oxidation of camphene with potassium permanganate, was cautiously melted in a silver crucible with potassium hydroxide. The thus resulting acid melted at 130 to 131° and did not cause any lowering of the melting point, when mixed with pure *d,l*-camphenic acid.

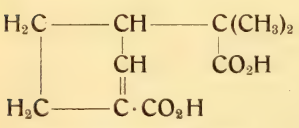
The lead salt of camphenecamphoric acid affords on distillation the corresponding ketone, which is identical with camphenilone[2]). As Lipp prepared camphenecamphoric acid synthetically, it follows that the production of camphenilone from camphenic acid represents a complete analysis of camphenilone. In consequence, it is beyond doubt that the formula as per margin expresses the constitution of camphenilone. The semicarbazone of camphenilone melts at 224°; camphenilone purified by way of the semicarbazone, at 36°.



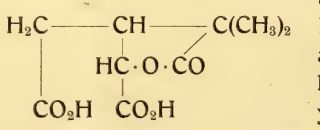
Camphenilone (α,α-dimethylnorcamphor).

On dry distillation of the calcium salt of camphenecamphoric acid no camphenilone resulted.

Dehydrocamphenic acid. Simultaneously and independently from each other, S. V. Hintikka and P. Lipp[3]) established for the lactonic dibasic acid, $C_9H_{12}O_6$ (m. p. 256°), which Aschan[4]) obtained by oxidizing dehydrocamphenic acid with nitric acid, the formula of a lactone of α-hydroxy*iso*camphoronic acid. This is opposed to Aschan's supposition, who looked upon this body as a lactone of α,α-dimethyl-β-hydroxyadipic-β-carboxylic acid. Lipp[5]) studied the subject further and found that *iso*camphoronic acid, on heating with bromine in a sealed tube until the bromine colour disappears, yields a product of the composition $C_9H_{12}O_6,H_2O$, melting at 185 to 186°. On further heating, a lactonic carboxylic acid, $C_9H_{12}O_6$, results (m. p. 253 to 254°). These two bodies proved in all their properties to be identical with the lactonic dibasic acid derived from dehydrocamphenic acid and its isomerides. Owing to this investigation, it may be taken for established that the body $C_9H_{12}O_6$ (m. p. 256°) from dehydrocamphenic acid really is the *trans*lactone of α-hydroxy*iso*camphoronic acid and that the stereomeric product (m. p. 185 to 186,5°) is to be regarded as the *cis*-modification.



Dehydrocamphenic acid.



Lactone of α-hydroxy*iso*camphoronic acid.

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[1]) *Berl. Berichte* **47** (1914), 1121. — [2]) G. Komppa and S. V. Hintikka, *Berl. Berichte* **47** (1914), 1550. — [3]) *Ann. Acad. Scient. Fennicae* A. **5** (1914), No. 3. — *Berl. Berichte* **47** (1914), 872. — [4]) *Liebigs Annalen* **375** (1910), 369; *Report* April **1911**, 188. — [5]) *Berl. Berichte* **47** (1914), 2994.

Hydroxycamphenilanic acid. On page 146 of our April *Report* of **1914**, we mentioned the preparation of hydroxycamphenylanic acid, as described by S. V. Hintikka. In a paper published later on, Hintikka[1]) reports fully on the production of this acid. He cautiously oxidizes camphene in aqueous acetone with potassium permanganate and removes the acetone, as well as the unaltered camphene and camphenilone by steam distillation. After evaporating the solution and extracting it with ether, he purifies the acid by way of the sparingly soluble sodium salt. It melts at 182°.

The 4 *isomeric acids*, $C_9H_{15}CO_2H$, resulting when camphene and bornylene are oxidized[2]), have been converted into their methyl esters by G. G. Henderson and M. M. Sutherland[3]). They are viscid, colourless liquids, which all boil at about 103 to 104° (22 mm.). The esters of camphenilanic, *iso*camphenilanic and camphenanic acids yield the corresponding acids when hydrolysed; however, on hydrolysis of the supposed ester of *iso*camphenanic acid, a mixture of camphenilanic and *iso*camphenilanic acids was obtained. It seems therefore that *iso*camphenanic acid consists of a mixture of camphenilanic and *iso*camphenilanic acids, or that it is converted into these acids during the formation of the esters.

On being treated whith sodium and alcohol, each of these esters furnishes camphenilanol, $C_9H_{15}\cdot CH_2OH$, a crystalline mass, melting at 77°. Chromic acid mixture oxidizes camphenilanol to camphenilanaldehyde. The hydrogen phthalate of camphenilanol melts at 153°; the *p*-nitrobenzoate, at 90°.

During the reduction of each of the esters, small quantities of *iso*camphenilanic acid are formed. Camphenilanic and camphenanic acids may therefore in this way be transformed into *iso*camphenilanic acid.

Pinic acid. When reducing pinic and norpinic acids according to Bouveault and Blanc, J. Östling[4]) obtained the corresponding glycols, boiling at 166 to 167° (16 mm.) and 138 to 140° (15 mm), respectively. They afforded dibromides melting at 144 to 145° (10 mm.) and 126 to 128° (10 mm.), respectively. Dimethyl and diethyl *d*-camphorate which had been prepared by means of methyl and ethyl sulphate, were likewise reduced, when a glycol (b. p. 158 to 160° at 16 mm.) and a hydroxy acid were formed, the methyl ester of which boiled between 145 and 146° (14 mm.).

Ascaridolic acid. The resolution of *i*-ascaridolic acid[5]) was carried out by E. K. Nelson[6]). He found that the cinchonidine salt of the dextro-rotatory modification is less readily soluble in hot water than that of the laevogyrous one, so that it is easy to separate the two salts from each other. The *d*-acid shows $[\alpha]_{D24^\circ} + 13{,}93^\circ$ (8,218 p.c. solution in chloroform); the *l*-acid, $[\alpha]_{D24^\circ} - 13{,}77^\circ$ (8,172 p.c. solution in chloroform). Both acids melted at 129 to 130°; the inactive acid melts at 117°.

Cyanolauronic acid. W. Borsche and W. Sander[7]) tried to prepare the chloride of cyanolauronic acid by distilling *iso*nitrosocamphor with phosphorus pentachloride; however, no pure product resulted, but a mixture of chloride and of nitrile of camphoceenic acid. In order to prepare pure chloride, the authors started from pure cyano-

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[1]) *Ann. Accd. Scient. Fennicae* A. **5** (1914), No. 3. From a reprint kindly sent us. — [2]) Comp. *Report* October **1911**, 134; April **1912**, 170; April **1914**, 130. — [3]) *Proceed. chem. Soc.* **30** (1914), 203. — [4]) *Chem. Ztg.* **38** (1914), 944. — [5]) Comp. *Report* October **1911**, 114. — [6]) *Journ. Americ. chem. Soc.* **36** (1914), 2551. — [7]) *Berl. Berichte* **48** (1915), 117.

lauronic acid, which they converted with the aid of thionyl chloride, into the chloride melting at 99°. They obtained cyanolauronic acid by saponifying the crude chloride. When reducing the nitrile of camphoceenic acid with palladium and hydrogen, camphoceanic acid nitrile (m. p. 28 to 30°) resulted, which on saponification was transformed into camphoceanic acid.

Oxydes.

On page 13, we have reported on dicitronelloxide, $C_{20}H_{34}O$.

Nitrogenous Bodies.

We mentioned at the time the conversion of the hydrazine compounds of citral and citronellal, as described by N. Kishner[1]), and can now give further details concerning this reaction. Kishner[2]) resolved a hydrocarbon, which he had obtained on heating citralhydrazone with potassium hydroxide, into two fractions boiling at 162 to 163 and 163 to 165° (760 mm.), respectively. These hydrocarbons correspond perhaps with the limonene and terpinolene forms of citral. When shaken with fuming hydrobromic acid the lower boiling hydrocarbon forms a compound which is isomeric with the raw material, *viz.*, linaloolene, $C_{10}H_{18}$. By reduction according to Sabatier it is converted into *i*-2,6-dimethyl octane, $C_{10}H_{22}$, melting at 159,5° (776 mm.). *d*-2,6-dimethyl octane results on reduction of the hydrocarbon, obtained from the hydrazone of citronellal.

W. Schneider together with D. Clibbens, G. Hüllweck, W. Steibelt and F. Wrede[3]) continued, his work on mustard oils and allied bodies[4]). He now reports on thiourethanes and thiourethane ethers from some natural mustard oils, synthetic glucosides from thiourethanes, the addition of phenol to mustard oils and on the phenylthiourethane-*d*-glucoside. They carried out the transformation of the silver allylthiocarbaminate with different halogen alkyls and further prepared a number of homologous and isomeric allyliminothiolcarbonates from the addition products of methyl and propyl alcohols with allyl mustard oil, obtaining as an intermediate stage the silver salts of these thiourethanes, which had not been described so far. Experiments were made as to the behaviour of allyliminothiolcarbonate towards silver nitrate and towards myrosine, as this ester has in its constitution certain relation to Gadamer's formula for sinigrine[5]). Myrosine does not influence the ester; silver nitrate decomposes it, but in a complicated way, under the formation of a mixture of insoluble silver salts, the principal constituent of which seems to be mercaptane silver. Further, thiourethanes of benzylmustard oil and of cheiroline[6]) were prepared. In order to obtain benzylthiourethane (ethylbenzylthiocarbaminate, $C_6H_5 \cdot CH_2 \cdot NH \cdot CS \cdot OC_2H_5$), 15 g. of benzyl mustard oil were heated in a tube for 6 hours up to 120 to 130° with 80 cc. of alcohol. With a view to obtaining the thiourethane quite pure, it must be distilled in an extreme vacuum. It boils at from 125 to 130° (0,3 to 0,4 mm.); the silver salt melts at 179°. If this salt is boiled with ethyl iodide, it affords diethylbenzyliminothiolcarbonate, $C_6H_5 \cdot CH_2 \cdot N{:}C(SC_2H_5)(OC_2H_5)$, boiling at 164 to 165° (18 mm.). When heated under pressure with absolute alcohol cheiroline forms a thiourethane, melting at 71°, *viz.*,

[1]) Comp. *Report* April **1912**, 195. — [2]) *Journ. russ phys. chem. Ges.* **45** (1913), 1779; *Chem. Zentralbl.* **1914**, I. 1497. — [3]) *Berl. Berichte* **47** (1914), 1248, 1258, 2038, 2218. — [4]) Comp. *Report* October **1910**, 85; April **1913**, 107, 151; April **1914**, 98. — [5]) Comp. *Report* April **1913**, 151. — [6]) Cheiroline is the sulfonic mustard oil occuring in wallflower seeds.

ethyl (methylsulphopropyl)-thiocarbamate, the silver salt of which melts at 150° and which on being boiled with ethyl iodide passes into diethyl (methylsulphopropylimino)-thiolcarbonate.

Through the action of acetobromoglucose on the thiourethane silver salts in chloroform, it was possible to synthesize the tetraacetyl compounds of the three glucosides from allylthiourethane (I), the thiourethane of cheiroline (II) and from benzyl-thiourethane (III). Unfortunately it was impossible to obtain the glucosides free from acetyl in an absolutely pure state.

(I) $C_3H_5 \cdot N : C(OC_2H_5) \cdot S \cdot C_6H_7O_5(C_2H_3O)_4$
Tetraacetylallylthiourethane glucoside.

(II) $CH_3 \cdot SO_2 \cdot (CH_2)_3 \cdot N : C(OC_2H_5) \cdot S \cdot C_6H_7O_5(C_2H_3O)_4$
Tetraacetyl glucoside from cheirolinethiourethane.

(III) $C_6H_5 \cdot CH_2 \cdot N : C(OC_2H_5) \cdot S \cdot C_6H_7O_5(C_2H_3O)_4$
Tetraacetylbenzylthiourethane glucoside.

The free thiourethane glucosides are very sensitive towards saponifying agents.

The authors further succeeded in proving that phenol cannot only be added to phenyl mustard oil, but likewise to allyl mustard oil, when thiourethanes are formed according to the scheme: $R \cdot N : CS + C_6H_5 \cdot OH = R \cdot NH \cdot CS(OC_6H_5)$. The addition takes place slowly already at room temperature, more quickly on heating the equimolecular mixture to about 80°. When being treated with ammoniacal silver solution, the phenylthiourethanes afford silver salts of their pseudo-modifications: $R \cdot NH \cdot CS(OC_6H_5) \longrightarrow R \cdot N : C(SAg)(OC_6H_5)$, a quality which may be employed with success for the isolation and purification of thiourethanes, as they can be obtained by decomposing the silver salts with hydrogen sulphide. Phenyl phenylthiocarbaminate, $C_6H_5 \cdot NH \cdot CS(OC_6H_5)$, melts at 142° and decomposes in contact with water little by little into phenol and phenyl mustard oil. It is prepared by conducting hydrogen sulphide into the silver salt of phenyl phenylthiocarbaminate, dissolved in chloroform. Said silver salt is obtained by heating equimolecular quantities of phenol and phenyl mustard oil up to 80° and afterwards adding silver nitrate solution to the well-cooled solution; it melts at 186°. The silver salt of phenylallylthiocarbaminate, obtained in the same way, melts above 140°; the phenylallylthiocarbaminate, at 51°.

It finally remains to discuss the synthesis of phenylthiourethane-*d*-glucoside, which shows great relationship with the natural mustard oil glucosides. The silver salt of phenylthiourethane reacts with acetobromoglucose, forming a tetraacetylthiourethane glucoside according to the equation:—

$$C_6H_5 \cdot N : C\begin{matrix} SAg \\ OC_2H_5 \end{matrix} + Br \cdot C_6H_7O_5(C_2H_3O)_4 = C_6H_5 \cdot N : C\begin{matrix} S \cdot C_6H_7O_5(C_2H_3O)_4 \\ OC_2H_5 \end{matrix} + AgBr$$

Phenylthiourethane silver. Acetobromoglucose. Tetraacetylthiourethane glucoside.

On saponifying the acetyl groups with alcoholic ammonia, phenylthiourethane-*d*-glucoside is obtained in addition to acetamide. As regards hydrolysis, this glucoside stands half way between the thiourethane glucosides synthesized hitherto and the natural mustard oil glucosides (sinigrine, glucocheiroline). Whereas the thiourethane glucosides, which are aliphatically substituted at the nitrogen molecule, decompose under the formation of urethanes and thioglucose, and the mustard oil glucosides are split up into glucose, mustard oil, and potassium pyrosulphate, the hydrolysis of phenylthiourethane-*d*-glucoside goes on in two directions, *i.e.* under the formation of

phenylurethane and thioglucose (IV) and, at the same time, similar to the decomposition of mustard oil glucosides, under separation of the sulphur from the sugar, when phenylurethane is formed again (V).

(IV) $C_6H_5 \cdot N{:}C\begin{cases} S \cdot C_6H_{11}O_5 \\ O \cdot C_2H_5 \end{cases} + H_2O = C_6H_5 \cdot NH \cdot CO(OC_2H_5) + C_6H_{11}O_5SH$

Phenylthiourethane-*d*-glucoside. Phenylurethane. Thioglucose.

(V) Phenylthiourethane-*d*-glucoside $+ H_2O = C_6H_5 \cdot NH \cdot CS(OC_2H_5) + C_6H_{12}O_6$

Phenylthiourethane. Glucose.

Phenylthiourethane-*d*-glucoside affords, on treatment with silver nitrate, on the one hand the silver salt of thioglucose, but on the other it forms again the silver salt of phenylthiourethane. This shows the relationship between the synthetic glucosides and natural glucosides from mustard oil, which latter are on this treatment split into mustard oil silver sulphates in addition to glucose. It is noteworthy that myrosine has no perceptible influence on the spontaneous decomposition of phenylthiourethane-*d*-glucoside.

The supposition, that the constitution of natural mustard oil glucosides in the sense of Gadamer's formula is to be derived from a hypothetical iminothiolcarbonic acid, receives an important support through these investigations.

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17

SEMI-ANNUAL REPORT

on

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Contents.

	Page
Introduction	5
Scientific and other notes on essential oils	7
New Pharmacopoeias	44
Chemical preparations and drugs	51
Notes on scientific research work in the domain of terpenes and essential oils	
General	55
Bibliography	56
Analytical	56
Physical	62
Botanical	64
Phyto-physiological	68
Pharmaco-physiological	69
Chemical	72
Hydrocarbons	77
Alcohols	79
Aldehydes	80
Ketones	82
Phenols and Phenol ethers	85
Acids	86
Oxides	86
Nitrogenous bodies	87

List of abbreviations.

d = specific gravity.
$d_{20°}$ = specific gravity at 20° (in references from our laboratories uniformly compared with water at 15°).
$d_{\frac{4°}{4°}}^{20°}$ = specific gravity at 20°, compared with water at 4°.
$\alpha_{D20°}$ = optical rotation at 20°, in a 100 mm. tube.
$[\alpha]_D$ = specific rotation.
$n_{D20°}$ = refractory index at 20°.
sol. p. = solidifying point.
m. p. = melting point.
b. p. = boiling point.
n = normal.
acet. = acetylation.
acid v. = acid value; ester v. = ester value; sap. v. = saponification value.
g. = gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

Miltitz near Leipzig, October 1915.

Unfortunately our present *Report* still labours under the restrictions which we had to impose upon it since the beginning of the war. In our last *Report* (October 1914/April 1915) we fully explained the reasons for our action, and once again we have to ask our readers to be satisfied in the main with a scientific review covering the last six months, as, with a few exceptions, we must refrain from publishing the usual particulars concerning the trade in our products until the re-establishment of peace. Statistical material will then be brought up to date as far as possible or necessary.

In a general way we may say our industry has also succeeded, as others have done, in adapting itself rapidly to the exceptional circumstances created by the war, and in spite of many difficulties, chief amongst which was the procuring of certain raw materials, our works were as fully occupied as was possible in view of the scarcity of labour which resulted from the fact that numerous members of our staff were called to the colours. At the same time it affords us a grim sort of satisfaction to observe how severely the absence of certain supplies of German manufacture has been felt abroad, in neutral as well as in alien enemy countries, and to realize that, in spite of German competition having been shut out during the 14 months the war had lasted at the time of penning these lines, our enemy competitors have evidently failed to perfect their methods sufficiently to jeopardize the future prospects of German goods in the markets which are closed to us for the present.

Numerous proofs could be adduced for this, f. i. from the pages of the English technical press, and a simple juxtaposition of the prices of German and foreign markets since war broke out would show how, apart from many essential oils, more especially artificial floral oils and certain other preparations have reached prices in the markets of our enemies which put everything into the shade. We do not, however, judge it wise to draw the special attention of our opponents to the range of articles we have in mind by enumerating the various products. Needless to say, our enemies, and more especially England, are trying through the intermediary of neutral foreign countries to procure articles of German manufacture which they cannot produce nearly as well as we can here in Germany, and the limits which are sanctioned, and even offered, shew as clearly as need be that they are compelled to accept even offers the prices of which are out of all proportion to the values still current in Germany in spite of the war and all it implies. The threat so frequently uttered in our alien enemies' press, that Germany would be completely cut off from its foreign markets until the re-establishment of peace, need not, therefore, be taken too tragically, at all events not as far as our articles are concerned.

In spite of their ostrich politics our enemies ought to have learned, from the results of the first year of the war, that a successful commercial crusade against Germany is out of the question, in spite of the various measures devised to throttle our foreign trade. The organization of labour, and its adaptation to existing circumstances, has been carried out to the fullest extent in Germany, whereas England, France and Russia have tried in vain to attain this object. In this way the panic-like events in internal economic life, about which we hear so frequently in the hostile press, are prevented with us. The favourable result of the third war loan surprised no one in Germany, seeing that it is fully realized that all payments for the army and the navy are bound to find their way back into home circulation, which means that no anxiety is, and need be, felt within our frontiers concerning the financial strength of the Nation.

We have every reason to continue our trust in the absolute justice of our cause, the bravery of the German and allied armies and the oft-tried ability of their leaders.

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Scientific and other Notes on Essential Oils.

Almond Oil, bitter. Concerning alteration, upon ageing, of amygdalinase and amygdalase, see page 69.

Anise Oil. On page 49 of our previous *Report* we mentioned a paper by Auguet on the determination of essential oils in absinth and other liqueurs, by Hübl's iodine absorption method. Similar examinations have been carried out since then by E. Morin[1]) and R. Marcille[2]).

When determining anise oil in Anisette, Morin invariably obtained figures which were too high. In order to ascertain the cause of this difference he determined Hübl's iodine value in solutions containing 0.8, 1 and 1.2 g. of anise oil per litre of 50 p.c. alcohol. Calculated on anise oil he found values corresponding with 1.651, 1.7018 and 1.7356, or an average of 1.6961. This figure differs considerably from the value of 1.391 found by Morin in technical literature, but it agrees with the number 1.640 established for anise oil by Barenthin. The figure 1.6961 found by Morin should only be made use of in cases where the liqueurs under examination contain about 1 g. of anise oil per litre.

According to Marcille the determination is influenced not only by the concentration of the anise oil but also by the strength of the alcohol. He suggests that the alcoholic strength of the liqueurs should be brought to 50 p.c., by the addition of more alcohol or water, as the case may be. Special care should be taken to add the iodine solution in the dark, and to allow the testing vessels to stand in the dark while the reaction takes place.

Bay Oil. In one of our previous *Reports*[3]) we gave a description of the bay oil industry in St. Thomas. In a complementary way we may here add a few notes on the bay leaf industry in the West Indies[4]). In order to ascertain whether the time of reaping the leaves has any influence on the properties of the oil, leaves were collected monthly from an experimental plot, and distilled separately. It was found that, in accordance with experiences collected at earlier dates, the leaves are richest in oil in the months of June and July. Phenol content as well as density of the oil are considerably influenced by the degree of maturity of the leaves; for instance, mature leaves distilled in December 1913 yielded an oil of the density of 0.9491, and containing 62 p.c. of phenols, whereas an oil obtained in January 1914 from young leaves showed a phenol percentage of 33 p.c. and a density of 0.8856.

To facilitate the reaping of the leaves, bay trees should not be allowed to grow higher than about 6 to 7 feet. The leaves are dried for a few days in covered sheds, before being distilled; whether this is of any use has yet to be ascertained.

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[1]) *Annal. de Chim. anal.* **20** (1915), 49. — [2]) *Ibidem* 52. — [3]) *Report* April **1913**, 31. — [4]) *Perfum. Record* **5** (1914), 425.

The question as to whether relations exist in bay oil between phenol percentage and specific gravity is ventilated in a short note published in an English contemporary[1]) from which it would appear that the specific gravity does not permit of any conclusions being drawn as regards the amount of phenols present in the oil. Several factors are presumably responsible for this, on the one hand the proportions of the various bodies contained in bay oil besides eugenol, but also the well-known readiness of myrcene to resinify. To cite but a few of the examples mentioned: three Dominica oils containing 24, 52 and 60 p. c. of eugenol respectively showed specific gravities of 0.960, 0.924 and 0.974 respectively, in other words figures which render any speculation about the one or the other constant impossible.

Buchu Leaf Oil. On page 9 of our previous *Report* we mentioned an essay by E. Goulding and O. Roberts[2]) on the leaf oil of *Barosma venusta,* referred to in the *Chemisches Zentralblatt.* The original paper now being at our disposal, we are able to communicate the following complementary notes: The mother-plant occurs in considerable quantities in the Uitenhage district of Cape Colony. The myrcene was identified by its constants as well as by the reduction product (dihydromyrcene) and its conversion, by hydration with sulphuric and glacial acetic acids, to an ester which resembled linalyl acetate in odour. Anisaldehyde was oxidized to anisic acid (m. p. 183 to 184°), linalool to citral (naphthocinchoninic acid derivative), methylchavicol being converted to anethole. Goulding and Roberts could not prove the existence of chavicol, of which body, according to Jensen[3]), the oil contains 16 p. c.

A new kind of buchu leaves is described in the *Perfumery and Essential Oil Record* [5 (1914), 373]. They originate from *Barosma scoparia,* E. et Z. and are very similar to the leaves of *Barosma venusta* (see above). The oil has a characteristic, pleasant odour; it does not appear to contain any buchu camphor.

Cajuput Oil. On the determination of cineol in cajuput oil, see page 20 of this *Report.*

Calamus Oil. In order to free the high-boiling parts of Japanese calamus oil from methyleugenol, Y. Asahina and E. Imaï[4]) treated these parts with Grignard's reagent; it was found by Simonis and Remmert[5]) and by Späth[6]) that this is capable of splitting off alkyl from phenol ethers, with reconversion of the phenol after the formula: —

$$C_6H_5OCH_3 + CH_3MgI = C_6H_5OMgI + C_2H_6$$
$$C_6H_5OMgI + H_2O = C_6H_5OH + MgIOH$$

The calamus oil ($d_{15°}$ 0.9820; α_D + 24.6°) examined by Asahina and Imaï contained 13 p. c. of methoxyl. Grignard's reagent (consisting of 2.4 g. magnesium, 11.4 g. of ethyl bromide and some absolute ether) was allowed to act on 40 g. of a fraction of the b. p. 120 to 140°[7]), containing 8.5 p. c. of methoxyl. The mixture was carefully heated; at 170 to 180° a fairly violent reaction set in, along with the formation of a

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[1]) *Perfum. Record* **6** (1915), 33. — [2]) *Journ. Chem. Soc.* **105** (1914), 2613. — [3]) Comp. *Report* April **1913**, 34. — [4]) Yakugakuzasshi of Nov. 1914, p. 1; *Journ. de Pharm. et Chim.* VII. **11** (1915), 299. — [5]) *Berl. Berichte* **47** (1914), 269. — [6]) *Monatsh. f. Chem.* **35** (1914), 319; *Berl. Berichte* **47** (1914), 766. — [7]) The pressure is not stated in the abstract.

brownish-black mass. This was agitated with dilute sulphuric acid and distilled with steam; the oil obtained in this process was dissolved in ether and treated with alkali in order to eliminate the phenols. After removal of the ether by distillation, the oil was fractionated over sodium *in vacuo,* in which process a part of the composition $C_{15}H_{24}$ and the b. p. 138 to 140° (31 mm.) distilled over; $d_{20°}$ 0.9379; α_D — 2.06°; $n_{D19°}$ 1.51009; mol. refr. 65.06, calculated for $C_{15}H_{24}$ 64.65. We seem to have to deal with a *tri*cyclic sesquiterpene. The rotation being low, the authors seem to be inclined to think that the oil may have become partly inverted by the treatment with Grignard's reagent. When oxidizing a part of the oil of b.p. 160 to 170° (containing 11.2 p.c. of methoxyl) with permanganate of potash, asarylaldehyde (m. p. 114°) was obtained, from which the presence of asarone may be assumed, which had been established at an earlier date in calamus oil by Thoms and Beckstroem[1]).

Camphor Oil. On account of the low prices ruling in 1914 owing to the cheap sales of Japanese camphor in Europe and America, business showed no profit to the Chinese producers[2]); consequently but little crude camphor was brought to the Chinese markets and the turnover remained within narrow limits. From Shanghai 1659 piculs, worth 132535 H. T., were exported in 1914, as against 1539 piculs of a value of 115887 H. T. in 1913.

The camphor tree *(Cinnamomum Camphora)* has been successfully planted in Burma, Ceylon and the Federated Malay States[3]). In Burma there are plantations in the upper Chindwin, Myitkyina, Bhamo and in the southern Shan States. There are experimental plantations in the Nilghiri Hills and in certain isolated patches of the Bombay and Madras presidencies. In Ceylon the tree grows only in the more elevated districts, one plantation being located in Hakgalla. It has always been found exceedingly difficult to procure good seeds imported direct from Japan. The seeds sown for the Burma plantations were obtained from Hongkong.

On repeated occasions we mentioned in our *Reports* the cultivation of camphor trees in northern America[4]). It now appears from a communication published by the Dept. of Agriculture[5]) in Washington that a syndicate of manufacturers of nitrocellulose products has about 500 acres under cultivation in Satsuma Heights (Florida) and has already obtained 10000 lbs. of crude camphor therefrom. Although the yield does not come up to expectations, it is hoped that this branch of industry may be further developed in a satisfactory manner. Three more companies are also working on the same lines, two in Florida and one in Texas.

Caraway Oil. According to the report of the Dutch Ministry of Agriculture of the middle of July, 3858 hectares were under caraway this year (about 9500 acres). This means a very considerable decline in cultivation as compared with the two years immediately preceding, for in 1914 5285 hectares, and in 1913 even 5527 hectares had been planted with caraway. It follows that one had to reckon with a considerable shortage of this year's crop from the very start. Into the bargain, immediately before

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[1]) Comp. *Report* October **1901**, 10; April **1903**, 14. — [2]) *Chem. Ztg.* **39** (1915), 711. — [3]) *Journ. Soc. Chem. Industry* **23** (1914), 1226; Comp. Gildemeister and Hoffmann, *Die ätherischen Öle*, 2nd ed., vol. II, p. 472. — [4]) Comp. *Report* October **1906**, 19; April **1907**, 20; October **1907**, 26; October **1908**, 34; April **1909**, 23; October **1911**, 26. — [5]) *Zeitschr. f. angew. Chem.* **28** (1915), III. 478.

harvesting, cool and rainy weather set in, so that the fair hopes which could be entertained earlier in the season as regards quality of new caraway were not fulfilled; the new seed turned out fairly dark in colour and the oil content can only be styled as middling. If, nevertheless, prices did not come up to the expectations of the Dutch farmers, this has, naturally enough, to be attributed to the fact that the war has restricted the demand as well as the possibilities of export. However, the market must be looked upon as firm and the oil prices, which had to be raised repeatedly of late on account of the unfavourable exchange of Mark currency, will no doubt be maintained at their high level for the present.

On caraway and the volatile oil of caraway we have before us a voluminous paper by K. Zijlstra[1]), from which we cull the following particulars which may be of interest to our readers.

In his introduction the author points out that the properties of the caraway plant are little known and that most farmers have no idea as to the influences the good quality of caraway seed is dependent upon; many of them do not even know about the use of caraway. No experiments at improvement have been carried out with this plant, moreover, it would be a difficult task. So far high yield was the only thing aimed at, little care being bestowed on the percentage of oil contained in the seed, and its quality. The seed is merely judged by odour, size and colour.

According to Zijlstra, no adequate description of the caraway plant can be found in any one of the books on agriculture which, by the way, may be said of many other cultivated plants. The lack of a thorough working basis is felt more keenly, especially if it is necessary to distinguish different races of a cultivated plant. This is not the case with caraway, but it would not be improbable that the difference in yield and in the composition of the oils of different origins may by ascribed in part at least to the presence, i. e. existence of subspecies of caraway.

For an exhaustive botanical description of the caraway plant we must refer to Zijlstra's original treatise. We need only state that as synonyma for caraway (*Carum Carvi*, L.) he gives the following names: *Aegopodium Carum*, Willd., *Apium Carvi*, Crtz., *Bunium Carvi*, Bieberst., *Foeniculum Carvi*, Link, *Lagoecia cuminoides*, Willem., *Ligusticum Carvi*, Bth., *Seseli Carvi*, Lam., *S. Carum*, Scop. and *Sium Carvi*, Bernh.

Caraway is found not only in northern and central Europe as far as Spain and Italy, but also in the Caucasus, in Persia, Tibet, and Siberia. In northern America it does not grow wild; it is, however, found as an escape from cultivation, more especially in the northern and north-western districts.

The biology of the flowers of the caraway plant shews interesting but also very intricate conditions, the close study of which will be necessary for the execution of improvement experiments.

It cannot be ascertained with any degree of certainty as to when caraway was first cultivated in Holland. All that is known is that at the end of the 18th century caraway was cultivated in fairly considerable quantities. In official communications it is first mentioned in 1815 under the heading "fine seeds", and it was chiefly cultivated in Northern Holland. About the middle of last century, cultivation on a larger scale was begun, and in 1851 there appeared the first official communication about the size of the area under cultivation; at that time it amounted to 55 hectares (about 130 acres).

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[1]) Mededeelingen van de Rijks Hoogere Land-, Tuin- en Boschbouwschool, vol. 8. From a special print kindly placed at our disposal.

In 1870, caraway cultivation was commenced in Groningen, the result, however, was very moderate, due partly to irrational ways of cultivation. Better results were not obtained until experts from Northern Holland had been called in. Meantime Southern Holland, Zealand, Utrecht and Northern Brabant began to get interested in caraway. From 1879 to 1885, cultivation fell back, but nothing is known as to the causes. Since then other periods of decline had to be registered, f. i. in the years 1889 and 1899.

The author gives the size of the territory under caraway cultivation, down to 1915, for the whole of Holland as well as for the several provinces in the form of graphic tables. In 1911, 0.9 p.c. of the cultivated area of Holland was under caraway. Among commercial plants, caraway takes the second place, with 13.11 p.c. of the total, flax being first with 64.55 p.c.

Caraway requires a fertile, deeply worked soil, free from weeds, clay soil in preference. As sowing takes place very early in spring, harvesting not being expected before summer of the ensuing year, the process of sowing is usually carried out in March or April along with a cover crop. This cover crop must ripen early, for it is only after its removal that the young caraway plants can develop properly. Moreover, it must not grow too high, otherwise it would prove disastrous to the young caraway shoots.

As a general rule, peas, beans, mustard, as well as flax or oats with clover are chosen as cover crops. In that case flax or oats can be harvested the first year, green clover or clover seed the second, and caraway the third year. In the district of Oldambt (Groningen), spinach has been recognized in recent times as being an appropriate cover plant.

It has been found useful beyond doubt to sow caraway in rows about 40 cm. apart (about 16 inches). The ground must be well loosened, and weeding done thoroughly, for weeds not only damage the young caraway plants, but affect the crop inasmuch as grass seed is difficult to remove from caraway seed, the commercial value being thus reduced.

Many farmers resort to ploughing down caraway slightly towards winter, in order to protect the young plants against frost. This is, however, unnecessary, as caraway is not easily affected by a wintry climate; on the other hand, weeds can be largely removed by ploughing. Harrowing takes place early in spring, so as to prevent the plants from coming to the surface yellow, which would reduce their power of resistance.

Caraway can stand a fairly powerful nitrogenous manuring, up to 400 kg. per ha., spread over the autumn and the ensuing spring. Harvesting takes place between end of June and early July, as soon as the fruit begins to become brown on the umbels which were first to flower. If the crop is deferred, considerable loss is unavoidable, for the ripe seeds will drop out of the umbels. Caraway must be cut in the early hours of the morning, and only in wet weather may cutting be done at other hours of the day. Of late the mowing machine is much used in Holland, especially in districts where caraway abounds and where labour is scarce. The sheaves are allowed to lie in the fields for a day, until dry, when they are gathered into shocks. The sheaves are also dried on frames[1]).

Harvesting must be done very carefully, in order to avoid losses, for if the work is done in a careless manner, much seed will be shaken out of the sheaves. Threshing is mostly done by machine. The yield amounts to from 20 to 30 bags of 50 kg. per ha.

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[1]) Pictures reproducing caraway harvesting and caraway cultivation in Holland will be found in our *Report* April **1911**, on frontispiece as well as in the text, page 40.

(20 to 30 cwts. per about 2½ acres); in good caraway districts as many as 40 bags were obtained per 2½ acres.

The following table illustrates the importance of the trade in caraway seed during the last few years: —

Import and Export of caraway seed to and from Holland.

Year	Import	Export
1905	60 000 kg.	4 669 000 kg.
1906	77 000 „	5 952 000 „
1907	93 000 „	6 286 000 „
1908	275 000 „	5 429 000 „
1909	83 000 „	8 312 000 „
1910	50 000 „	6 149 000 „
1911	110 000 „	8 988 000 „
1912	94 000 „	4 298 000 „

The imports shewed the following figures: —

in 1911 total 109 970 kg., value fl. 26 392.—

of which from	Malta (?)	46 959 kg.
	Great Britain	31 785 „
	Germany	25 341 „

in 1912 total 94 209 kg., value fl. 15 410.—

of which from	Malta (?)	46 962 kg.
	Germany	27 571 „
	United States	15 044 „

The exports amounted to:

in 1911 total 8 988 081 kg., value fl. 2 157 139.—

of which to	Germany	4 342 109 kg.
	United States	2 714 019 „
	Great Britain	1 025 100 „

in 1912 total 4 297 847 kg., value fl. 1 031 483.—

of which to	Germany	2 407 477 kg.
	United States	1 027 289 „
	Great Britain	481 306 „

The caraway seeds originating from different districts of Holland showed differences as regards content and quality of the oil. In order to ascertain the causes it was necessary to determine oil content and quality of a considerable number of samples. Inasmuch as Zijlstra had but little material at his disposal, he chose the method indicated by Beckmann[1]) for the determination of oil percentage by ascertaining the depression of the freezing point. The carvone content of the oil he calculated from the refractory index.

As will be known, according to Beckmann's method the depression of an extract of comminuted seed, produced with ethyl bromide, is first determined, followed by determination of the depression of an extract of seeds from which the oil has first

[1]) *Arch. der Pharm.* **245** (1907), 211; *Report* October **1906**, 104; October **1907**, 114.

been eliminated by high-pressure steam. The difference of the two values corresponds to the depression caused by the volatile oil, from which the oil content may be easily calculated. On distilling the comminuted seeds according to the directions laid down by Beckmann, the unpleasant fact was noticed that the oil was decomposed in part. Zijlstra proved this by determining the refractory index of mixtures of limonene and carvone of known composition, before and after distillation (Beckmann's method), when considerable differences were found. This test was made with the Universal Refractometer of Abbe, for which purpose but a few drops of oil are necessary. Moreover, more than but a few drops are not obtained from the distillation of the 5 grams of seed used after Zijlstra's method. By means of a table the carvone content may be read off easily from the value for n_{D20°.

From caraway seed originating from different districts in Holland, oils were obtained, after Beckmann's distillation method, which showed very low figures for carvone, i.e., as low as from 7.5 to 25 p.c., which must be attributed to above-mentioned decomposition. By shortening the duration of distillation, and by using a little cylinder made of copper gauze instead of a tube of filtering paper as a receptacle for the distillation material, and finally by closing the little cylinder with a lid of the same material instead of a cotton-wool plug, Zijlstra succeeded in carrying out the distillation of carvone-limonene mixtures without an alteration in the refractory index becoming noticeable. From one and the same parcel of caraway seed, 27.0 p.c. of carvone were obtained after Beckmann's method, as against 51.5 p.c. after Zijlstra's modified method. The carvone content ascertained by determining the refractory index is invariably a little too low, but the differences are constant.

In the course of distillation a grey, emulsion-like mass collects in the condensing tube. This mass may possibly contain some fat oil (fixed oil). It must not be allowed to get into the distillate, as this would give rise to incorrect results. From caraway seed collected in 1910 in the Haarlem district, 4.65 p.c. of oil were obtained in this manner, showing 47.5 p.c. of carvone. As regards the particulars of the method employed, we must refer readers to the original treatise.

The author also examined 25 samples of caraway seed of the 1910 crop and found oil contents varying from 3.75 p.c. to 5.32 p.c.; the carvone percentage ranged between 47 up to 54.5 p.c. Wild caraway seed collected in Holland contained 5.75 and 6.72 p.c. of oil. It cannot be said with any degree of certainty to what causes these differences in oil and carvone percentages have to be attributed. It could, however, be proved by cultivation experiments that the distances from furrow to furrow exert a decided influence on the yield and oil percentage. For this purpose the author used Dutch caraway seed which contained 4.17 p.c. of oil showing 55.5 p.c. of carvone. The result of the experiments will be shown in the following table: —

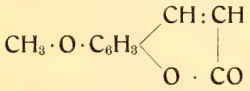
	Method of planting	planted	Oil content	Carvone content of oil	Yield in bags of 50 kg. per ha.
A)	Distance from furrow to furrow 30 cm.,	thickly	4.89 p.c.	51.5 p.c.	21.4
B)	„ 30 „	thinly	5.14 „	52.0 „	15.5
C)	„ 60 „	thickly	5.03 „	53.0 „	21.4
D)	„ 60 „	thinly	5.44 „	53.0 „	12.2

This table will show that the oil percentage of the harvested seed was greater than the oil percentage of the seed used for sowing. It is surprising that the yields of A and C are identical, although the number of caraway plants with C was only half that of A.

Further experiments were made with a view to ascertain whether it would be advantageous to plant foreign caraway seed of high oil percentage in Holland. For this purpose Zijlstra examined a number of samples of foreign seed for oil and carvone percentage. Thus he found, f. i., in wild caraway from Örebro (Sweden) 6.09 p.c. of oil showing 55 p.c. of carvone; Hamar (Norway) 6.79 p.c. of oil with 55.5 p.c. of carvone; Württemberg (Jagst district) 7.17 p.c. of oil with 53 p.c. of carvone. Lower values were found in samples from other countries, down to 3.36 p.c. of oil with 50 p.c. of carvone in caraway from Kasan (Russia). Cultivation experiments undertaken, with these samples showed that some sort of an adjustment had taken place: the differences in oil and carvone percentage were not as great and the seed produced resembled Dutch grown caraway seed. The above-mentioned caraway from Örebro yielded 4.65 p.c. of oil with 55 p.c. of carvone, Hamar seed 4.15 p.c. of oil with 55 p.c. of carvone, Württemberg seed 5.28 p.c. of oil with 56.5 p.c. of carvone, and Kasan seed 4.11 p.c. of oil with 54 p.c. of carvone. Thus the hope of obtaining seed rich in oil and carvone from the cultivation of similar seed of foreign origin has not been fulfilled.

Zijlstra believes that the indifferent results may have to be attributed to the existence of different kinds of *Carum Carvi;* if there are such kinds which do not grow satisfactorily in Holland, selection appears to take place.

Chamomile Oil. In the oil of chamomile flowers from *Matricaria Chamomilla,* L. (N. O. *Compositae*), F. B. Power and H. Browning jun.[1]) have proved the presence of furfurol by means of the usual colour reaction. After some little time a small quantity of a body melting at 110° deposited from the oil. On being heated it developed an odour like coumarin, the solution in concentrated sulphuric acid showing a blue fluorescence. It seems evident that this body is identical with umbelliferone methylether (herniarin)[2]), which melts at 117 to 118° in the pure state. So far it had only been found in burstwort *(Herniaria hirsuta,* L., N. O. *Caryophyllaceae),* but never before in essential oils. Umbelliferone is the lactone of umbellic acid, 2,4-dihydroxycinnamic acid; it is therefore 4-hydroxycoumarin.



Umbelliferone methylether.

It is not known whether umbelliferone methylether occurs also in chamomile oil produced in the normal way, for the oil examined by Power and Browning had been obtained as a by-product from the alcoholic extract of chamomile flowers by steam distillation. A fatty acid of the m. p. 61° was also found in the oil. Besides many other bodies the authors established the presence, in the alcoholic extract of chamomile flowers, of a paraffin melting at 63 to 65°, which proved to be triacontane, $C_{30}H_{62}$, as well as of a phytosterol, $C_{27}H_{46}O$, melting at 132 to 134°. Some time ago Klobb, Garnier and Ehrwein[3]) had obtained from chamomile flowers a hydrocarbon, for which they gave the formula $C_{29}H_{60}$.

Cinnamon Oil. According to Rosenberg[4]) this oil is said to be an excellent treatment for warts. It would appear that it suffices to apply one drop per day to the warts, when they will disappear within a few days without leaving any scar. The treatment is said to be entirely painless.

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[1]) *Journ. Chem. Soc.* **105** (1914), 2280. — [2]) Barth and Herzig, *Monatsh. f. Chem.* **10** (1889), 161. — [3]) Comp. *Report* April **1911**, 167. — [4]) *Amer. Medicine,* February **1915**; *Practitioner* **1915**, June. According to *Pharmaceutical Journ.* **94** (1915), 804.

Citronella Oil, Java. In spite of the difficulties under which shipments of large parcels from Java have to be made at the present time, we have obtained several consignments of superior quality and are at the disposal of interested parties for special offers. Seeing that Ceylon citronella has practically disappeared from German markets, we would like to draw our customers' attention to the fact that a good, unworked Java oil, such as we are in a position to supply, is nearly twice as powerful as, besides being of an infinitely and incomparably finer odour than, Ceylon oil. It can be strongly recommended in all cases where our Ceylon citronella substitute, introduced a few months back and well liked by most users, does not satisfy completely as regards fineness of odour.

Clove Oil. In a Netherland Colonial journal[1]), a treatise[2]) is discussed about clove cultivation in Zanzibar, from which we may here reproduce a few particulars in completion of previous communications[3]). The clove tree requires clay soil, the trees growing better on red or brown clay soil than on lighter coloured soils. Before sowing, the seeds are softened in water for about three days and, after germination has taken place, they are planted in shaded beds. The beds must be kept well watered and the shoots must be protected against the sun by being roofed over. The young plants remain in these beds from 9 months to a year; as soon as they are about 15 cm. (6 inches) high, the roofing is removed little by little, after which the plants remain in the sunny beds for another two months or so, when they are used for the plantations. The distance between the plants should be from 5.5 to 7.3 m. (6 to 8 yards). A round hole is dug, about 1.2 m. wide and 0.6 m. deep, in the centre of which there is a planting hole about 0.3 m. wide and deep. The planting has to be done with great care, and the young plants are watered in hot or dry weather, but in no case are they protected against the sun. It is assumed that the clove tree attains the age of about 90 years. It seems to be attacked but very rarely by fungoid diseases[4]), but it often happens that its leaves are devoured entirely by caterpillars; however, during the rainy season the foliage grows again. White ants also damage the tree occasionally by destroying the roots.

The Imperial Institute, of London[5]), has collected observations showing the content of oil in Zanzibar cloves in the various stages of development, and has examined the oils thus obtained. The following are the particulars of this examination: —

1. Cloves from a tree 8 to 9 years old.
2. Cloves from a tree 45 years old. The cloves were picked just before the buds turned pink, or about 8 to 10 days before ready.
3. Cloves from a tree 60 years old; the cloves were picked when the buds had become pink and ready for picking.
4. Cloves from a tree 60 years old, cloves picked when in full flower.
5. Mother-cloves from a tree 60 years old; sample consisted principally of clove fruits, but a considerable number of buds were also present.

Of Nos 1 and 2 the stems were also distilled. The result is shown in the following table: —

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[1]) *Indische Mercuur* **38** (1915), 471. — [2]) *Simmon's Spice Mill.* 1915, No. 42 of April 15th. — [3]) Comp. *Report* October **1910**, 39; April **1913**, 47; October **1913**, 45; April **1914**, 47. — [4]) Comp. page 65 of this *Report.* — [5]) *Bull. Imp. Inst.* **12** (1914), 337.

Sample	Yield of oil	$d_{15°}$	α_D	Eugenol in the oil
1.	17.8 p.c.	1.056	—0° 23′	89 p.c.
2.	19.2 „	1.064	—0° 30′	88 „
3.	18.8 „	1.049	—0° 29′	84 „
4.	17.4 „	1.050	—0° 37′	88 „
5.	6.5 „	1.056	—0° 33′	90 „
6. stems from sple. 1.	5.9 „	—	—	—
7. „ „ „ 2.	6.3 „	1.050	—0° 42′	89 „

As will be seen, yield as well as constants of the oils are within normal limits throughout. Strange to say eugenol percentage is lowest in the oil obtained from the cloves picked at the usual time. Even as regards odour this oil did not take first place by any means, it was surpassed by the oil from "unripe" cloves (N° 2). It is followed by the distillate from "ripe" cloves (N° 3), after which come the oils N^{os} 1 and 4. The least pleasant odour was shown by the oil from mother-cloves[1]), the oils from stems taking an intermediate position. Of the two stem oils, the one from the early cloves of older trees (N° 7) smells better than the oil from clove stems obtained from younger trees (N° 6).

It it worth noting that the cloves gathered early (N° 2) yielded not only the highest percentage of oil, but the best quality also.

The Imperial Institute is of opinion that no definite conclusion can be drawn from the above-mentioned single series of experiments, chiefly because the cloves originated, in part at least, from old trees of quite different ages. In order to ascertain definitely the effect of picking the cloves at different stages of development, it is desirable that samples should be collected from trees of the same age and not from trees of different ages. The effect of the age of the tree could be determined by collecting series of similar samples from trees of different ages.

Coffee Oil. We have reported before now[2]) on the volatile constituents of coffee. According to J. Abelin and M. Perelstein[3]), the volatile parts of coffee are affected by the air, the yellowish, liquid distillation residue becoming converted into an intensely brown, gelatinous mass. By means of alkalis the product is precipitated from the aqueous solution as a heavy, light coloured oil. A quantitative analysis revealed the presence of nitrogenous substances as well as of furfuralcohol.

This observation may possibly be looked upon as an explanation of the fact that coffee, which has been allowed to stand for some time, or coffee extract, does not possess the taste of freshly prepared coffee any longer.

Cubeb Oil. In a former publication, C. A. Hill and J. C. Umney[4]) had stated that with pure cubeb oil at least 80 p.c. should distil between 250 and 280°. This was modified at a later date, as Umney, in collaboration with E. T. Brewis[5]), had found that the fraction in question often amounted to but 64 p.c. of the oil, so that a requirement of 60 to 65 p.c. would probably be entirely satisfactory. A further contribution to this question is furnished by the firm of "Oranje"[6]) in Amsterdam. With four oils

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[1]) As regards the properties of an oil distilled by ourselves from mother-cloves, see page 53 of our previous *Report*. — [2]) Comp. *Report* October **1902**, 31; April **1913**, 49; October **1913**, 47. — [3]) *Münch. med. Wochenschr.* **61** (1914), 867; *Chem. Zentralbl.* **1915**, I. 908. — [4]) *Chemist and Druggist* **76** (1910), 271; *Report* April **1910**, 133. — [5]) *Perfum. Record* **5** (1914), 256; *Report* April **1915**, 17. — [6]) *Perfum. Record* **5** (1914), 372.

of their own manufacture from 72.2 to 86.4 p.c. distilled within the above-mentioned limits of temperature. The oils themselves had been obtained to the extent of 9.5 to 15 p.c. and showed the following constants: d_{15° 0.9233 to 0.9268; α_D — 27.4 to — 37.6°. Two of these oils contained no parts boiling below 250° at all, the remaining two showed 12.8 and 18.0 p.c. of such fractions respectively.

Essential Oils, Sicilian and Calabrian.

Lemon Oil. A novel and mysterious method for the manufacture of lemon oil has been worked out by Liotta[1]). The lemons are pounded in a large vessel and mixed with an acid, the composition of which is kept secret. This acid is said to produce the separation of the oil, which rises to the surface and is removed. A substance is then added which liberates the acid, so that it can be used again! The residue, consisting of lemon juice, pulp, peels, &c. is sold to manufacturers of citrate of lime.

It is said that with this new method the yield of oil is 2½ p.c. higher than with the old method of pressing by hand. As regards cost, this is said to be but 2.3 cents per 1000 lemons, the operation lasting only 22 minutes. By perfecting the method and by working on a large scale it is expected that the operation can be carried out within about 12 minutes.

As long as no further particulars are known about the mysterious acid and the substance used for recovering it, we may say this new method smacks somewhat of a fairy-tale.

Eucalyptus Oil. The resorcinol method published by us a number of years ago[2]) has on repeated occasions been the subject of criticism on the part of English chemists[3]). These gentlemen will not admit the method even in its modified form (determination of eucalyptol in the fraction boiling between 170 and 190°) on the pretext that it yields insufficient results. They base their verdict merely on the fact that they arrive at different results when separating the eucalyptol with phosphoric acid, but they fail to adduce proofs for the reliability of the phosphoric acid method. We have tested this latter method very thoroughly and have ascertained beyond doubt that correct results are obtained with it by accident only. Every unbiased observer who has handled the addition product of cineol separated from eucalyptus oil by means of phosphoric acid will agree with our statement. It would be like carrying coals to Newcastle, were we to revert to the subject once again at great length, suffice it to refer once more to what we said in our *Report* of October **1907**, page 46. On the other hand we have produced, in above-mentioned *Report* as well as in our *Report* of April **1908**, voluminous proofs of the resorcinol method being useful in its original form, if, besides cineol, chiefly hydrocarbons are present, such as is the case with oils of the amygdalina variety, whereas, if at the same time oxygenous bodies are present (alcohols, aldehydes) correct results are obtained if the fractions boiling between 170 and 190° are subjected to the modified resorcinol test. Quite acceptable values are

[1]) *Commerce Reports* No. 65 of the 19th of March 1915 (Washington). — [2]) *Report* October **1907**, 47; April **1908**, 50; Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 601. — [3]) Comp. *Report* April **1908**, 52; October **1910**, 67; April **1913**, 62.

obtained, as discussed on former occasions (*Report* April 1908, 50), if cineol is separated as a solid resorcinol compound and the latter decomposed; at all events as far as reliability is concerned, this method of determination is not in any way inferior to any method recommended in other quarters, and it has the special advantage of the addition product of cineol with resorcinol being the most easily handled of all these compounds.

Of late the resorcinol method has once again been checked by H. G. A. Harding[1]). Even with the modified method he obtained useful results only in cases where the cineol content did not exceed 50 p. c. Otherwise even here the results were found to be too high. He suggests that in cases of too high a percentage of cineol, fraction 170 to 190° should be diluted with turpentine oil to such an extent that the cineol content is reduced to about 40 p. c. The mixture is then to be shaken with hot resorcinol lye, which he uses in 55 p. c. strength. To obviate possible mistakes, he does not use ordinary turpentine oil for the dilution, but the fraction boiling between 156 and 160°.

As will be found from the figures published by us at the time, we arrived at correct results by the modified method, even with oils containing more than 50 p. c. of cineol.

A contribution to the determination of eucalyptol is furnished by J. L. Turner and R. C. Holmes[2]). They are of opinion that none of the methods proposed so far yield satisfactory results. The determination of the cineol percentage by means of phosphoric acid meets with difficulties, inasmuch as the addition product is of sticky consistency and decomposes very rapidly. The same may be said as regards the hydrobromic acid method, and the permanganate of potash method recommended by Dodge also proves ineffective (compare *Report* April **1913**, 62 and *Report* April **1915**, 71). The authors attack the resorcinol method more especially, because it has been suggested for inclusion into the new American Pharmacopoeia. They pretend that, even with the modified method, the results obtained are invariably too high, a statement about which there may be two opinions, seeing that we ourselves arrived at the opposite result, for which we produced experimental proof at the time. Be this as it may, Turner and Holmes are no doubt of a different opinion and have therefore cast about for a new test. In arsenic acid they believe to have found a compound which is far better suited to the quantitative analysis of cineol than all the other compounds suggested so far. The use of arsenic acid for separating cineol from eucalyptus oil and kindred articles is far from being novel, having been patented to the firm of Merck in Darmstadt in 1901 for the production of eucalyptol (D. R. P. 132606). Its use for quantitative determination of cineol was therefore indicated, and the only reason why, at the time, we had refrained from making use of it was that in arsenic acid we have to deal with a powerful poison, and because, moreover, we consider the addition product with resorcinol even more suitable. Of this fact we are fully persuaded to this day. There can be no doubt about it that for the purpose in question arsenic acid is far superior to phosphoric acid, but it is equally certain that at the very least equally satisfactory results are obtained by means of resorcinol.

For the test with arsenic acid, Turner and Holmes give the following directions:

"Deliver from a pipette 10 cc. of the oil into a glass dish of 50 cc. capacity, which is embedded in finely cracked ice. Add 10 cc. of concentrated arsenic acid (containing about 85 p. c. arsenic acid) and stir until precipitation is complete. When

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[1]) *Analyst* **39** (1914), 475; *Journ. Soc. Chem. Industry* **33** (1914), 1171. — [2]) *Perfum. Record* **6** (1915), 20. After a paper read at the November meeting of the New York section of the American Pharmaceutical Society.

the mixture ceases to congeal further, allow to stand 10 minutes in the ice. At this point, if the mixture forms a hard mass, indicating an oil rich in cineol, 5 cc. of purified petroleum ether should be added, and the mass mixed well. Transfer immediately to a hardened filter-paper by means of a pliable horn spatula, spread evenly over the surface of the paper, and lay a second hardened filter-paper over the top. Outside the hardened filter-paper place several thicknesses of absorbent or filter-paper and transfer the whole to an ordinary letter-press, bringing to bear all the pressure possible for about one minute. Change the outside absorbent papers and press again, repeating the operation, if necessary, until the cineol arsenate is apparently dry and separates readily when touched with a spatula.

The pressing is *not* complete when a hard mass remains which is broken up with difficulty. The method usually requires two changes of filter-paper, pressing each time for about two minutes. If left too long in the press, the compound may decompose. Now transfer completely the compound by means of the horn spatula to a glass funnel inserted into a 100 cc. cassia flask with neck measuring 10 cc., graduated in $^1/_{10}$ cc. Wash the precipitate into the flask with a stream of hot water from a wash-bottle, assisting the disintegration with a glass rod. Place the flask in boiling water and rotate until the compound is thoroughly broken up; add enough water to cause the cineol to rise into the neck of the flask, cool to room temperature and read off the volume; on multiplying the latter by 10, the percentage of cineol in the oil is obtained.

In judging whether or not petroleum ether should be added, the following rule should be observed: Add enough petroleum ether to soften the cineol arsenate, so as to obtain a plastic mass; the quantity necessary never exceeds 5 cc., and decreases with oils containing less than 80 p.c. of cineol. The object of adding petroleum ether is merely to soften the hard mass and to aid in the separation of non-cineol constituents of the oil; a large excess of petroleum ether will decompose the compound".

According to Turner and Holmes, the arsenic acid method is applicable directly to all oils containing more than 50 p.c. of cineol. With lower cineol percentages, the precipitate is not solid enough to permit convenient handling; if the cineol content drops below 25 p.c., separation of cineol arsenate is not quantitative. It was found that the addition of an equal volume of cineol to such oils successfully overcomes this difficulty. In the calculation it only becomes necessary to subtract from the volume of cineol, as observed in the neck of the flask, 5 cc. and to multiply the difference by 20[1]) in order to obtain the percentage of cineol in the oil.

The authors have tested this method with three different mixtures of cineol (50, 60, and 70 p.c.) with turpentine oil and have obtained correct results. Moreover, for comparison purposes they determined the cineol percentage of a number of oils with arsenic acid as well as with resorcinol, the test being carried out by the original as well as by the modified method. Unfortunately they make no mention as to the results obtained, so that it is impossible to see in how far these agree. As a proof that the arsenic acid method is superior even to the modified resorcinol method, they merely mention the constants of the cineol obtained in one way and the other and collected from several tests. For the cineol separated from the arsenic acid compound they found: m. p. $-1°$; $d^{25°}_{25°}$ 0.9218; $\alpha_D + 0°13'$, and for the one from resorcinol compound: m. p. $-3°$; $d^{25°}_{25°}$ 0.9242; $\alpha_D + 0°7'$. These differences, which are really trifling, they look upon as very important and they conclude from the agreement of the first-

[1]) In the Perfum. Record, 10 is given as factor. Needless to say this is incorrect, seeing that, according to the method described, only 5 cc. of the original oil had been treated.

mentioned cineol, in melting point and specific gravity, with the requirements of the American Pharmacopoeia, that it contains no other parts of eucalyptus oil any more. This, however, is a slight error, seeing that from the melting point[1]) as well as from the optical behaviour it can be seen that even the cineol regenerated from the arsenic acid compound is impure, although it has to be admitted that the impurities of the cineol originating from the resorcinol compound are a little more pronounced, as it has a still lower melting point. But in both instances the impurity is, comparatively speaking, trifling and does not permit of any conclusions being drawn as to how far the correctness of the results obtained in the cineol determination are influenced thereby, the less so as in the case of these cineols we have to deal with collective products from several determinations. The only correct course would have been to publish the results themselves.

From our own experiments, carried out with oils as well as with mixtures made in our laboratories, it is evident beyond doubt that resorcinol yields at least as good results as arsenic acid. We have worked on the one hand according to the modified resorcinol method, but on the other hand we also separated cineol as a solid resorcinol compound. When dealing with mixtures we did not confine ourselves merely to the most favourable cases, by simply mixing cineol with a terpene, but in two cases we added terpineol, i. e. an alcoholic constituent which has often to be reckoned with in oils to be tested, and by which the results are unfavourably affected. Consequently mixtures of this nature form a far better standard valuation for checking a certain method, than if cineol be merely diluted with a terpene. In the following table we have collected the results of our experiments.

No.		Arsenic acid method		Resorcinol method	
		with addition of petroleum ether	without addition of petroleum ether	Shaking the fraction 170 to 190°	Isolating and decomposing the solid cineol-resorcinol compound
1.	Cineol . . . . . 80 p.c. Limonene . . . . . 20 „	73 p.c.	80 p.c.	—	80 p.c.
2.	Cineol . . . . . 50 „ Limonene . . . . . 50 „	—	48.5 „	—	49 „
3.	Cineol . . . . . 50 „ Limonene . . . . . 25 „ Terpineol . . . . . 25 „	13 p.c.	13 „	52 p.c.	20 „
4.	Cineol . . . . . 60 „ Limonene . . . . . 30 „ Terpineol . . . . . 10 „	—	53 „	62 „	53 „
5.	Eucalyptus oil, Globulus . . .	70 p.c.	82 „	87 „	83 „
6.	Cajuput oil	—	53 „	63 „	53 „

Several points may be gathered from the figures obtained by us. To begin with, it is shown that, when testing with arsenic acid, the use of petroleum ether is inadvisable, seeing that even with a high cineol content the values obtained are too low,

[1]) Pure eucalyptol melts between + 1 and + 1.5° (comp. *Report* October **1907**, 49); the indication of the U. S. P. is not correct.

whereas correct results are obtained if petroleum ether is discarded. The same may be said of a content of only 50 p.c. of cineol, if besides this only terpene is present. But if alcoholic constituents are present at the same time, the method fails either completely (No. 3), or the results remain considerably behind the actual values (No. 4).

Similar observations may be made if cineol is isolated in solid form by means of resorcinol, and the compound decomposed. This method of separation is not in any way inferior to the arsenic acid process, on the contrary, the latter way yields even worse results, if Turner and Holmes' directions are strictly adhered to by mixing the cineol arsenate with petroleum ether. As regards the handiness of the addition products with arsenic acid on the one hand, and with resorcinol on the other hand, we have made the observation that with mixtures consisting only of cineol and hydrocarbons, separation takes place equally well with both methods, but that in the presence of alcohols the arsenic acid compound takes decidedly longer to form, consequently it is more difficult to obtain than the one with resorcinol, and compares unfavourably with the latter on account of its sticky consistency.

Thus even under such experimental conditions the resorcinol method is not excelled by any other test, and the results become even considerably better if the modified method is applied, by shaking the fractions 170 to 190° with a 50 p.c. resorcinol solution[1]). By this method we have again and again obtained excellent results, so that we can strongly recommend this way of determination, for in spite of all the statements to the contrary it is very useful and, as far as reliability goes, it is undoubtedly far superior to all other methods, including the arsenic acid method. The only drawback is, perhaps, its requiring comparatively much oil, a consideration which has induced us to study the question from a new point of view. As the resorcinol method in its original form yields too high values if oxygenous compounds are present, and as the latter are mainly of an alcoholic nature, it is but natural to assume that useful results might be obtained by direct shaking of the oil with resorcinol lye, if at the same time the percentage of acetylizable constituents is determined, deducting it from the part of the oil dissolved in the resorcinol, after its percentage has been established. The difference should represent the actual cineol content. As will be seen from the following table, we have succeeded in obtaining satisfactory values in this manner. The calculation of the alcoholic constituents was based on the formula $C_{10}H_{18}O$. As was done in the experiments enumerated in the first table, terpineol was chosen as alcohol for the mixtures, this being a natural constituent of cajuput oil. In this manner a reliable opinion may be formed as to how the results obtained from natural oils are to be valued. Acetylation was carried out in the usual way with undiluted oil, as well as in the manner prescribed for terpineol (5 hours' acetylation, the oil being diluted with four times the amount of xylene. Gildemeister, *The Volatile Oils*, 2nd ed., vol. I, page 578). The differences throughout were so trifling that, for the sake of saving time, acetylation in the usual way may be chosen without having to fear that appreciable mistakes may be brought about. It may also be left out of consideration that the percentage by shaking is established volumetrically, by acetylation gravimetrically. The resulting difference only amounts to fractions of one per cent; a correction which might be based on the specific weights is, therefore, not necessary. We now come to the results: —

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[1]) The proposal by Harding, mentioned on page 18, to use hot resorcinol lye for the shaking process is quite acceptable, seeing that in this way an easier and quicker separation of the yet undissolved oil parts from the lye may be effected. However, there is no reason for an alteration in the concentration of the solution.

No.		Original resorcinol method: shaking of the oil found:	Acetylisable parts of the oil, calculated for $C_{10}H_{18}O$ found:	Difference = real cineol percentage of the oil	Modified resorcinol method: shaking fraction 170 to 190° found:
1.	Cineol . . . . . 50 p.c. Limonene . . . . . 25 „ Terpineol . . . . . 25 „	76 p.c.	27 p.c.	49 p.c.	52 p.c.
2.	Cineol . . . . . 60 „ Limonene . . . . . 30 „ Terpineol . . . . . 10 „	70 „	10 „	60 „	62 „
3.	So-called Australian Eucalyptus oil	17 „	8 „	9 „	10 „
4.	Eucalyptus oil, Globulus	92 „	5 „	87 „	87 „
5.	Cajuput oil	80 „	15 „	65 „	63 „

Further experiments will be necessary to establish in how far this modification is useful in the examination of oils. We would therefore recommend it only conditionally for the present.

As regards Turner and Holmes' statements, referred to on a previous page, it is satisfactory to note that they characterize the phosphoric acid method, so much vaunted by a few English chemists, as useless, an opinion which we held from the first, and which, according to the *Perfumery and Essential Oil Record* [**6** (1915), 206] was reproduced in recent times in *The Chemist and Druggist of Australasia.*

The fact that the Australian oil of *Eucalyptus globulus* satisfies the requirements of the U. S. Pharmacopoeia, but not the Californian oil, has induced C. E. Burke and C. C. Scalione[1]) to examine the composition of Californian oil more closely. They found the oil to contain the same constituents as the Australian oil but in other proportions. The yield from fresh leaves was 0.8 p.c.; $d_{20°}$ 0.9052; $[\alpha]_{D20°}$ 14.42° (+ ?); $n_{D20°}$ 1.46053; insoluble in 70 p.c. alcohol; acid v. 0.73; sap. v. 2.5; ester v. after acet. 56.0. The raw material used in California mostly consists not only of leaves from *Eucalyptus globulus*, but also of a sprinkling of other varieties. The authors examined the oil obtained from such material. It was found to contain butyraldehyde and *iso*valeraldehyde, which yielded ammonia addition products of the m. p. 26 to 27° and 52 to 53°, respectively. In a fraction of the b. p. 100 to 140°, capronaldehyde was probably present. α-Pinene (d- ?) was characterized by the determination of the physical properties and the preparation of the nitrosochloride (m. p. 102 to 103°). Cineol was found to the extent of 47 p.c. (phosphoric acid method). Eudesmol and globulol could also be established without difficulty[2]). Eudesmol showed the molecular refraction 68.001, whereas a sesquiterpene alcohol $C_{15}H_{26}O$ requires 68.069. This amounts to a confirmation of Semmler's opinion, according to which eudesmol is an unsaturated sesquiterpene alcohol, and not an oxide as suspected by Baker and Smith. The quantitative composition of the oil may be about as follows: 6 p.c. aldehydes, 21 to 22 p.c. pinene, 47 p.c. cineol, and 23 p.c. of alcohols. It is probably due to the high percentage of pinene that the oil does not come up to the requirements of the U. S. Pharmacopoeia.

[1]) *Journ. Ind. Eng. Chemistry* **7** (1915), 206. — [2]) Comp. *Report* October **1913**, 56, 57.

From the buds 0.2 p.c. of an oil was obtained, same being specifically lighter than the oil from the leaves.

Eupatorium Oils. The genus *Eupatorium* (N. O. *Compositae*) comprises more than 500 species, 56 of which occur in the United States. From three species only *(capillifolium, triplinerve* and *aromaticum)* oils are known to have been produced[1]). Now a detailed paper by E. R. Miller[2]) on the oil of *Eupatorium capillifolium,* (Lam.) Small. (*E. foeniculaceum,* Willd.) has come to hand. The raw material had been collected in Auburn (Alabama). In the course of 11 years, Miller has distilled altogether about 30 samples which were all laevo-rotatory, whereas the oil described by us some time ago shewed dextro-rotation. The oil is nearly colourless or light yellow. Yield 0.8 to 1.35 p.c. from freshly collected herb; $d\frac{25°}{25°}$ 0.9278 to 0.9472; α_D — 3.7 to — 16.8°; $n_{D20°}$ 1.50055 to 1.50688; acid v. 0.18 to 0.25; sap. v. 10.92 to 13.67; soluble in about 0.7 vol. of 90 p.c. alcohol, on more being added opalescence sets in. The oil showed but traces of aldehydes and ketones and perhaps a little salicylic acid. By means of a methoxyl determination the presence of a phenol ether was established, which proved to be thymohydroquinone dimethylether (b. p. 244°) and formed the main constituent of the oil. On treatment with concentrated hydriodic acid it yielded thymohydroquinone (m. p. 142°), which was oxidized to thymoquinone (m. p. 44 to 45°). On distilling the oil with alcohol, a fraction was isolated which contained terpenes of a low specific gravity (as low as 0.8295 at 25°) and phellandrene (nitrosite, m. p. 96 to 98°; 100 to 101° and 111 to 114°). Pinene and sabinene could not be ascertained, neither does linalool appear to belong to the constituent parts of the oil, but borneol was found to be present and was characterized by oxidation to camphor (oxime). In the saponification lye of the oil acetic acid (silver salt) as well as some other volatile acids were present.

From the herb of *Eupatorium purpureum, hyssopifolium* and *perfoliatum* no oils, or but traces only, was obtained, on the other hand *Eupatorium serotimum,* a species occurring in the eastern parts of the United States, yielded 0.51 p.c. of oil (calculated on the undried herb); $d_{25°}$ 0.9075; acid v. 0.5; sap. v. 28.7; sap. v. after acet. 61.92; soluble in 0.5 vol. of 90 p.c. alcohol, on addition of 1.7 vol. the solution became opalescent. The oil was of fairly dark colour, so that a determination of the rotation was impossible. Presumably it contained traces of salicylic acid and seemed to consist chiefly of sesquiterpenes.

Geranium Oil. In Limaru (British East Africa), geranium oil has been distilled recently from fresh herb[3]). As mother-plant a variety (perhaps *quercifolium*) of *Pelargonium radula* is mentioned. The properties of the oil are: d 0.890; α_D — 10°; $n_{D25°}$ 1.4706. it contains 9.6 p.c. of geranyl acetate.

Oil of Helichrysum saxatile. According to L. Francesconi and R. Sernagiotto[4]), *Helichrysum saxatile,* Moris (N. O. *Compositae*) yields an oil of a peculiarly acrid, though fairly pleasant odour, reminding of roses. d 0.9020; α_D — 11.71°; n_D 1.4769. The bulk distils at 240° and appears to contain a body belonging to the group of hydroaromatic substances, possibly an oxygenous sesquiterpene derivative. Aldehydes and ketones were not present in the oil.

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[1]) Comp. Gildemeister and Hoffmann, *The Volatile Oils,* 1st ed., p. 667; *Report* April **1904**, 96; April **1907**, 106; April **1908**, 17. — [2]) Bulletin of the University of Wisconsin No. 693. Madison (Wisc.) 1914. — [3]) *Perfum. Record* **5** (1914), 423. — [4]) *Gazz. chim. ital.* **44** (1914), II. 419; *Chem. Zentralbl.* **1915**, I. 835.

Hop Oil. Schmidt[1]) reports on two hop plants cultivated in Carlsberg ("Oregon cluster" and "New York spaulding English cluster"), the hops of which showed a pronounced turpentine odour. By crossing experiments it was proved that the turpentine-like aroma was transmissible to from $^2/_3$ up to $^3/_4$ of the descendant plants. From these and several other experiments it would appear as though the hop aroma could not be looked upon as being of such transient nature as is generally assumed.

It may here be called to mind that, according to Rabak[2]), American hop varieties are not exactly famous for fineness of aroma.

Iva Oil. In our *Report* April **1912** (page 83) we gave a few particulars, on the properties and composition of iva oil which can now be completed by publishing the constants of an oil we distilled ourselves about a year ago. It was very similar to the oil reported on previously: $d_{15°}$ 0.9339; $n_{D20°}$ 1.47632; acid v. 5.6; ester v. 24.3; ester v. after acet. 86.8; soluble in 0.8 vol. of 80 p.c. alcohol; on more being added, paraffin was separated. The yield was 0.41 p.c. The original blue-green colour had turned to olive-green in the course of time.

Oil of Kaempferia Ethelae. The Zingiberacea *Kaempferia Ethelae,* J. M. Wood, grows freely in north-eastern Transvaal; its dried bulb, which is called *"Sherungulu"*, is said to possess medicinal properties. When distilling 31.8 kg. of these bulbs, E.Goulding and O. D. Roberts[3]) obtained 1.5 p.c. of oil, whereas another distillation, carried out in the Imperial Institute in London with a smaller quantity of bulbs, only produced 1.1 p.c. The oil is a pale yellow, readily mobile liquid of a faintly orange-like odour, with a hardly pleasant by-odour reminding of crushed ivy leaves. The oil obtained by Goulding and Roberts consisted of 93 p.c. of light, and of 7 p.c. of heavy parts.

The light oil shewed: $d_{15°}$ 0.9437; $\alpha_{D22°}$ + 19° 47′; acid v. 2.3; ester v. 5.0; ester v. after acet. 47.6. It contained dipentene (tetrabromide, m. p. 124°) and perhaps also pinene, furthermore cineol (iodol compound, m. p. 112°), traces of free acid (acetic acid?) and phenols of creosote-like odour, linalool (oxidation to citral; citrylidenecyano-acetic acid, m. p. 120 to 121°), methylanthranilic acid (m. p. 179°; presumably this acid is present in the oil in the form of methylester) and a new ketone $C_{24}H_{28}O_4$. It is contained in the parts boiling above 135° (20 mm.), i. e. 270° (ord. pressure), from which it separates in colourless crystals at ordinary temperatures. Recrystallized from alcohol it melts at 102° and shows $[\alpha]_{D22°}$ + 198° 20′ in chloroform solution. The crystals are colourless to start with, but soon become brown on exposure to the air. In concentrated form the ketone is nearly odourless, but dissolved in dilute alcohol it smells of crushed ivy leaves. It reacts neither with neutral sodium sulphite nor with sodium bisulphite. Attempts at oxidation produced no results; methoxyl or ethoxyl groups could not be proved. With hydroxylamine hydrochloride and a slight excess of sodium hydroxide, the ketone formed a hydroxylamino oxime of the m. p. 184°, which, when shaken with dilute acetic acid, was converted into the oxime m. p. 166°. It is readily hydrolyzed with hydrochloric acid. Benzoylation after Schotten- Baumann yielded a benzoyl derivative of the m. p. 260°. On boiling with alcoholic N/2 potassium hydroxide lye, the ketone is converted into an amorphous powder of the m. p. 200°.

The heavy part of the oil contains mainly the ketone, and perhaps also some sesquiterpenes.

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[1]) *Wochenschr. f. Brauerei* **32** (1915), 109. — *Compt. rend. du Lab. de Carlsberg* (3) **11**, 316; *Chem. Zentralbl.* **1915**, I. 1212. — [2]) Comp. *Report* April **1915**, 27. — [3]) *Journ. Chem. Soc.* **107** (1915), 314. — *Bull. Imp. Inst.* **13** (1915), 15.

The composition of the oil is as follows: 21.8 p.c. of terpenes, 17.2 p.c. of cineol (resorcinol method), 13 p.c. of a ketone of the m.p. 102°, 11.2 p.c. of alcohols (including linalool), 1.3 p.c. of ester (including methyl methylanthranilate), 0.5 p.c. of phenols, 0.1 p.c. of acids, and 34.9 p.c. of high-boiling parts, mainly sesquiterpenes.

Oil of Lagoecia cuminoides. E. M. Holmes[1]) reports on the oil from *Lagoecia cuminoides*, L., an umbellifera of deviating structure, as is clearly visible from the pictures with which the article is illustrated; it occurs in the eastern Mediterranean countries. The oil contains carvacrol, but Holmes does not state how he has proved this body in the oil, nor does he give any indications as to the constants of the oil.

Lavender Oil. The numerous kind enquiries from our various friends as to the fate of our lavender oil distilleries in Barrême (Basses-Alpes) and Sault (Vaucluse) afford us the opportunity to inform enquirers that all we know are a few paragraphs culled from newspapers, from which it is evident that since the beginning of the war both establishments were sequestrated by the French Government. Fortunately our stocks of lavender oil had already been shipped to us here when war broke out, and as in both places we employ native labour only, none of our staff suffered any loss or inconvenience.

Under the heading of "Lavender robbers", the *Berliner Tageblatt*[2]) published a noteworthy article, running as follows: "In its last leader the official Paris trade journal *Le Bulletin* complains about the fact that, from indolence and lack of spirit of enterprise on the part of the natives, the Germans had been allowed to invade the special domain of France, viz., the perfumery industry, and in continuing the discussion of the question it raised the query whether it was not time to call into existence, in the districts suitable for the purposes, French factories, exactly after the pattern of the sequestrated German establishments, and fitted up in exactly the same perfect style. In the reports on these points we read the following: For a number of years the Germans have made systematic attempts to bring the production of aromatic plants in France into their power, more especially in the departments of Vaucluse and Basses-Alpes. They have succeeded, needless to say exclusively to their own advantage, to bring about an enormous rise in the prices of lavender oil which is chiefly produced in these districts, this genuine French article which is exported every year in considerable quantities to England, the United States and to Germany. To the detriment of our own native perfumery distillers, the Germans have insinuated themselves into two districts specially famous for the quality of their aromatic plants, viz., in Barrême, in the Basses-Alpes and in Sault, in the department of Vaucluse. In order to dispel the mistrust which met them, the Germans showed themselves much more liberal towards the old-established guileless herb-gatherers than did their competitors, and as the intruders disposed of considerable capital it was easy for them to secure every year large quantities of the very best floral material for the requirements of their highly developed establishments. In 1902, fr. 15.— per kilo was paid on an average for pure lavender oil. The procedure of the Saxon factories established in Sault and Barrême has driven prices little by little to fr. 38.— and has therefore produced a quite unjustified rise by 100 p.c., which is naturally felt in a very unpleasant manner by the French perfumery industry. Thus we see that in less than ten years the Germans have succeeded in drawing from their industry a profit of many millions, by the rise created by them in

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[1]) *Perfum. Record* **6** (1915), 231. — [2]) No. 84, evening edition of February 15th, 1915.

the prices of lavender oil and they can, therefore, easily bear the losses caused them by the probable liquidation of the distilleries sequestrated by the Government in the Basses-Alpes and in Vaucluse. It must be admitted that they have understood how to obtain in their admirably equipped factories, under the direction of excellent chemists, large quantities of essential oils from the abundance of wild growing plants, and they have thereby succeeded in capturing a considerable part of our exports in these articles. It will be the duty of men with patriotic minds and business-like initiative to bring about a change in this state of affairs and thus to render a great service to their country. To begin with, it will be advisable to follow the example of the Saxon distillers in many respects. Their all-powerful establishments in the Provence are a cruel lesson to our indolent industry, which seems to be devoid of initiative. It would be incredible if we were not to derive immediate profit from this lesson, the more so as our farmers have proved a hundred times that very considerable returns can be made from a scientific cultivation and distillation of medicinal and aromatic herbs. Now is the time to interest the inhabitants of the more and more depopulated and poor regions of the southern French Alps and of the Cevennes in the indroduction of rationally worked cultivations of officinal herbs and plants for the production of essential oils which grow better there than anywhere else. Next it would be our business to establish, after the style of the splendidly equipped German distilleries, French factories in the heart of these floriferous districts. For it has been proved that oils distilled on the spot from cultivated plants are as a rule far superior in strength to those obtained from wild growing plants. Lavender oil, which is used in the manufacture of a vast number of perfumery products, and also medicinally, cannot be replaced by any synthetic product, it is therefore a very important article of commerce, at home as well as for our export. Is it not our duty to try to keep this business in French hands?"

We have replied to this article in the *Parfümerie-Zeitung*[1]) and avail ourselves of this opportunity to give a copy of it to those of our readers who may not have seen the number of the journal in question.

We said:

"It may be premised that by the establishments "of Saxon distillers" our lavender oil factories in Barrême (Basses-Alpes) and Sault (Vaucluse) are aimed at, as there are no other factories of similar importance in German hands. Our Barrême factory was erected in 1905 on our own soil and has since then been enlarged and perfected as deemed necessary from the experiences gathered in the handling of fresh lavender flowers, until it has reached a state of perfection in its inner workings and its output capacity which has no equal in southern France. In normal years, such as f. i. in 1912, 500000 kilos of lavender flowers were distilled for essential oil, the distillate obtained being of a quality never before attained (ester content about 52 p. c.). In another central place in the lavender producing districts, in Sault (Vaucluse), we also worked since 1905 in a hired factory, with equally excellent results as regards quality.

Every reader will have to admit that, taken as a whole, the vituperations of *Le Bulletin* are really rather flattering to us, seeing that the author speaks of "factories spendidly equipped by excellent chemists", and in another place of "splendidly equipped German distilleries". These statements are now made, though during the last few years no means was left untried to thoroughly spoil our pleasure in the success of our creations. Among these means there ranks, in the first place, the positively astonishing cleverness, by an incredible distortion of facts, in arousing the suspicion

[1]) **1** (1915), 8.

of consumers of lavender oil, an article which is used more or less in almost every perfumery and soap factory, by pretending that the considerable rise in prices which the lavender oil market experienced during the last two years had been brought about solely by our entering the circle of the southern French distillers. It was said that the lavender-gathering population had been made more independent by our granting disproportionately high prices for flowers year by year, and that the perfumers and soapmakers had to thank us for having to pay higher prices now than twenty years ago. It would lead too far, were we to touch upon this question once again. We have often enough had to refer to it in the various editions our *Semi-annual Report* during the last few years, to which we can refer those of our readers who are interested in the polemic in question. The true fact is, however, that the Frenchmen, and they alone, are the guilty parties, for their blind fury against the "German intruders" has always found expression in their steadily and invariably outbidding our buyer, an expert gentleman, native of southern France, and devoted to us, in his negotiations with the flower gatherers, or contractors, with a view to make it impossible for him to secure the quantities of flowers necessary to keep our establishments going. Much to the disgust of our adversaries we have more than once simply stopped our purchases of flowers, the result being that the hotspurs in question were saddled with their dear flowers whereas we, by erecting and fitting up a few flying (ambulant) distilleries, in places where flowers were to be had in abundance and cheaper than in the immediate neighbourhood of our own distilleries, were able to cover our requirements more advantageously. We may here point out with satisfaction and recognition that a few serious firms among the number of our southern French competitors were ready to come to an understanding with us, the result being that the prices to be offered to the gatherers were mutually agreed upon. In this way we succeeded in silencing at least a part of the hotheads. If 1913 had not brought a short crop and if, in 1914, owing to the sudden outbreak of the war, we had not been compelled to stop work in these factories, these arrangements would surely have produced more favourable conditions as regards prices, for the 1914 crop promised to be very good. But the calling to arms of the major part of the working population will most likely have had the result that the crop could not be brought in entirely, and that distillation will have been within very narrow limits. To make matters worse, the considerable production of the whole of our plant had to be left out of the calculation this time.

As we have seen from French newspapers, our two factories in Barrême and Sault have been sequestrated by the French Government. What will happen? "The men of patriotic minds" will have found little difficulty in gaining admission to our establishments, they will have studied the plant according to all the rules of the art, they may possibly destroy everything emanating from Germany and vent their fury on the "lavender robbers" by establishing similar factories in all suitable places, in order to drive us away definitely. It is just possible that these gentlemen might meet with the disappointment that they cannot find "those excellent chemists" to guide and direct the latest creations of the French spirit of enterprise. But even if everything were to work satisfactorily, and if the Frenchmen succeed in producing qualities similar to ours, we shall only be glad in the interest of our numerous friends in the perfumery trade. We never erected our factories down there in order to "gain millions", as mentioned in the vituperations under discussion, but chiefly with a view to bring about a general improvement of quality by the introduction of modern and really scientific distillation methods. It is hardly flattering to the Frenchmen that it required the energy of German "lavender robbers" to teach them in their own country how lavender oil should be

distilled in accordance with all the rules of the art. It is only through our own endeavours that it has at last become known what lavender oil should really be, and that the method of distillation in vogue in the South of France is really quite wrong, inasmuch as it decomposes the most valuable constituent of lavender oil, namely, linalyl acetate. A further advantage, moreover, which our appearance in the South of France has brought about to the consumers of lavender oil consists in the fact that adulteration with oil of spike, which had been practised on a very large scale formerly, has decreased very much of late, because private distillers are now bent on supplying oils as high in ester percentage as possible.

In any case we venture to advise the gentlemen with "commercial initiative" to try to behave like civilized beings, lest the "settlement" to be presented after the conclusion of peace become a little more than they bargained for."

Several years ago F. Elze[1]) proved the presence of thymol in lavender oil. When discussing the publication at the time[2]) we pointed out that thymol might have got into the lavender oil examined by Elze accidentally, and that it could be decided by an examination of guaranteed pure material only whether thymol really belonged to the list of normal constituents of lavender oil. Meantime we have had an opportunity of carrying out such an examination. We had to deal with an oil distilled by ourselves from French lavender grown in Miltitz. When cutting the flowers, special care was taken to avoid any foreign herb getting mixed with the lavender flowers: we thus obtained an absolutely pure lavender distillate, which had the following constants: d_{150} 0.8912; α_D — 3° 57′; acid v. 1.5; ester v. 87.7 = 30.7 p.c. linalyl acetate, soluble in 2.5 vol. and more of 70 p.c. alcohol. For the determination of thymol we proceeded in the same way as Elze, by agitating the oil repeatedly with a 3 p.c. caustic soda lye, saturating the collected alkaline liquids with carbonic acid, and extracting them with ether afterwards.

After evaporating the ether, Elze obtained a residue which smelled of thymol and, after boiling *in vacuo* and placing in ice water, became solid when inoculated with a small thymol crystal. In our own oil, of which we dealt with about 10 kilos (roughly 22 lbs.), we failed to prove even a trace of thymol. It may therefore be assumed that thymol does not occur in pure lavender oil, and that the oil examined by Elze originated from flowers which had become accidentally mixed with a herb containing thymol (thyme herb).

Oil of Limes. In an article by W. R. Dunlop[3]) on limes and lemons as raw material for the manufacture of citric acid and essential oils, we find a few particulars on the cultivation of limes in the West Indies, regarding which we had reported on previous occasions[4]). The lime tree grows best on flat or only slightly hilly ground, in protected spots, up to an altitude of about 250 m. (about 825 feet) with a yearly average rainfall of about 2000 to 4000 mm. (about 80 to 160 inches). In the West Indies, where the lime tree grows best, the average temperature is about 27° in the shade (about 80° F.). The seedlings are mostly planted out about 4.6 m. apart (about 5 yards), in case of need the soil should be drained; special attention is devoted to the planting of wind belts (wind breakers). In the West Indies the seedlings are usually supplied by the local Agricultural Departments, of late, however, a few estates have started raising their own seedlings. As regards manuring, hardly

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[1]) *Chem. Ztg.* **34** (1910), 1029. — [2]) *Report* April **1911**, 78. — [3]) *Bull. Imp. Inst.* **13** (1915), 66. — [4]) Comp. *Report* April **1913**, 73; October **1913**, 70; April **1914**, 68.

any experiences have been collected, but it is no doubt of advantage to impart much humus substance to the soil. Generally speaking, the lime tree suffers but little from insects or fungoid diseases. After five years the first crop may be gathered, in the eighth or tenth year the yield is at its best. The tree bears fruit for about forty years. In Dominica and St. Lucia the principal crop takes place from June or July to November or December. The fruit requires about 6 months to attain maturity, the yield amounting to about 24000 lbs. of fruit per acre. Fruits which are to be worked up for lime juice, citrate of calcium and essential oil are allowed to remain on the tree until they drop. Before the limes are pressed for the manufacture of juice and citric acid, they are usually ecuelled[1]) or pressed by hand. The inferior distilled oil is obtained in the process of concentrating lime juice. The lime contains more juice and citric acid than the lemon, but less essential oil.

Mustard seed Oil. Under the designation of "wild mustard" the wholesale trade in America handles a mixture of the seeds of *Brassica arvensis* ("Charlock") and of *Brassica juncea* ("brown mustard"); this is a by-product obtained in very large quantities in the process of cleaning cereals and flax; it is said to be shipped to Europe. A. L. Winton and J. H. Bornmann[2]) have determined the oil percentage of various samples of this product, finding values ranging between 0.26 and 1.13 p. c. In the seeds of *Brassica arvensis* they found 0.15 and 0.25, in those of *Brassica juncea* 2.89 and in the seeds of *Brassica nigra,* used for comparison purposes 4.62, in *Brassica alba* (white mustard), however, only 0.16 p.c. of volatile oil. The oil percentage of "wild mustard seed" depends therefore on its botanical composition. The oil can only be used for technical purposes.

A critical treatise on the most important methods for examining mustard seed oil will be found on page 56 of this *Report.*

Concerning the influence of *o*-toluidine on allyl mustard oil we refer to page 88 of this *Report.*

Origanum Oil. When, some time back, E. M. Holmes received origanum plants from Cyprus, where they are used in the distillation of oil of Cretic *Origanum*[3]), an *Origanum* species called *"Rikhanon"* in Cyprus was sent him. As it proved to be different from everyone of the known species of *Origanum,* Holmes[4]) called it *O. Bevani,* after its discoverer. In its habits it resembles *Origanum smyrnaeum* and also shows some similarity with *O. syriacum,* but it differs in the formation of its calyx and the hirsuteness and colour of its leaves. Holmes' article on the subject is illustrated by a photograph of the flowering plant.

Oil of Paeonia Moutan. A new synthesis of paeonol is described on page 86.

Peppermint Oil, American. About the crop of the year 1914 we have now before us an exhaustive report which, though belated, we would like to submit to our readers. Favourable weather in the months of March and April had greatly assisted the growth of the plants and as, into the bargain, the area placed under peppermint

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[1]) The "écuelle à piquer" is an instrument which was used formerly in the manufacture of agrumen oils in Nice; it consists of a bowl, lined with upright brass spikes; the bowl is supplied with a tube at the bottom. — [2]) *Journ. Ind. Eng. Chemistry* **7** (1915), 684. — [3]) Comp. *Report* October **1913**, 75. — [4]) *Perfum. Record* **6**(1915), 19.

cultivation was 3600 acres larger than in 1913, there was every reason to look forward to a good result of the distillation. Our New York expert, despatched, as every year, into the peppermint districts of Michigan and Indiana, reported quite favourably on the development of the fields; but as the 1913 stocks had been entirely used up by spring 1914, the favourable prospects were unable to exert a weakening influence on the prices; on the contrary, good oil fetched no less than $ 4.25 per lb. But when, towards the end of June, distillation began unusually early and when it was found that, in consequence of the favourable weather conditions, the yield was exceptionally heavy, amounting to as much as 30 lbs. per acre, and that therefore a total result of 550 000 to 600 000 lbs. would have to be reckoned with, prices could not be maintained any longer, but receded to as low as $ 1.50 in the course of the year. Besides, the quality of the oil was very good, for the farmers had benefitted so liberally from the high prices ruling during the few months preceding the crop that, needless to say, they had bestowed particular attention on the care of their fields and had spared neither labour nor money to make the most of the coming crop. In consequence of the war, however, exports of the oil were almost completely stopped, an improvement of the prices was therefore not to be hoped for as long as no conclusions could be drawn concerning a possible crop failure in 1915. There were no reasons for such anticipations during winter 1914 and spring 1915. But at the beginning of the distilling season in July this year heavy rains set in, the fields were sadly devastated, the yield was reduced and in some districts the herb rotted. To make matters worse, on account of the exceptionally favourable weather two cuts had been made almost without exception last year, in consequence of which the plants were weakened in 1915 more than they would have been after a less favourable crop. A rise in prices was, however, avoided as there were again 3600 acres more under peppermint than in the preceding year, besides, export business was in a bad way on account of the continuation of the great war. At the time of writing this report the prices were about $ 1.55 to $ 1.65 per lb. With it all the consumption of peppermint oil is said to have increased to such an extent that of the very considerable yield of 1914 only about 100 000 lbs. remained unsold. From this it is surmised that higher prices may rule between now and next crop, unless we were to meet with unfavourable reactions in American home trade, caused by the influences of the European war.

According to personal observations of our expert, the districts under peppermint in the years 1913 to 1915 are as under: —

1913 to 1914.

Michigan.

Counties	1913	1914 newly planted	1914 total
Van Buren Co.	1650 acres	1356 acres	1967 acres
Cass Co.	1427 „	594 „	1524 „
Berrien Co.	1317 „	313 „	1249 „
Allegan Co.	1395 „	369 „	893 „
Gratiot and Montcalm Counties	614 „	576 „	877 „
Saginaw Co.	950 „	600 „	850 „
St. Joseph Co.	348 „	377 „	538 „
Kalamazoo and Calhoun Counties	464 „	273 „	526 „
Eaton Co.	260 „	162 „	290 „
Branch Co.	102 „	129 „	207 „
Total for Michigan:	8527 acres	4749 acres	8921 acres

Indiana.

Counties	1913	1914 newly planted	1914 total
Steuben Co.	70 acres	40 acres	80 acres
Noble and Whitney Counties	201 „	224 „	411 „
Elkhart Co.	300 „	447 „	696 „
Lagrange Co.	1192 „	670 „	1547 „
St. Joseph Co. and neighbourhood	5055 „	3114 „	8921 „
Total for Indiana:	6818 acres	4495 acres	10090 acres
Total for Michigan:	8527 „	4749 „	8921 „
Total for Michigan and Indiana together:	15345 acres	9244 acres	19011 acres

Excess in 1914 against 1913: 3666 acres.

1914 to 1915.

Michigan.

Counties	1914	1915 newly planted	1915 total
Van Buren Co.	1967 acres	785 acres	2607 acres
Cass Co.	1524 „	269 „	1569 „
Allegan Co.	893 „	558 „	1321 „
Berrien Co.	1249 „	150 „	1349 „
Saginaw Co.	850 „	300 „	850 „
St. Joseph, Branch, Kalamazoo and Calhoun Counties	1271 „	290 „	1371 „
Gratiot and Montcalm Counties	877 „	183 „	1052 „
Eaton Co.	290 „	53 „	315 „
Total for Michigan:	8921 acres	2588 acres	10434 acres

Indiana.

Counties	1914	1915 newly planted	1915 total
St. Joseph, Laporte, Stark and Marshall Counties	7356 acres	1421 acres	8567 acres
Elkhart and Kosciusko Counties	696 „	325 „	996 „
Lagrange Co.	1547 „	524 „	2071 „
Steuben, Noble and Whitney Counties	491 „	110 „	524 „
Total for Indiana:	10090 acres	2380 acres	12158 acres
Total for Michigan:	8921 „	2588 „	10434 „
Total for Michigan and Indiana together:	19011 acres	4968 acres	22592 acres

Excess in 1915 against 1914: 3581 acres.

Oil of Peppermint, rectified, "Miltitz 1914". We avail ourselves of this opportunity once again to draw our readers' attention to this novelty, which we introduced by special circular last January. As it was to be expected that the stocks of English Mitcham peppermint oil, which in view of the proximity of the crop were not very considerable when war broke out, would become exhausted before long in Germany, we have tackled the task of producing a complete substitute for the benefit

of the numerous users of the English oil, the more so as no German nor Austro-Hungarian consumer can be expected to use English peppermint oil in future. We always maintained that English Mitcham peppermint oil was greatly overvalued, and our exhaustive practical experiments have justified this opinion beyond doubt. By resorting to a special fractionating and rectifying process, the peppermint distilled in the United States from Mitcham plants will produce an oil which can be looked upon as a full substitute of the English distillate. Away therefore with English Mitcham peppermint oil from German and Austro-Hungarian recipes and prescriptions! Expert opinion which has reached us so far confirms our statement that our new quality is really a complete substitute for the English oil. Needless to say it comes up to the all the requirements of the German Pharmacopoeia.

Peppermint Oil from British East Africa. A peppermint oil obtained from Mitcham plants in Molo (British East Africa) showed the following properties: d 0.967; α_D — 33° 30′. Total menthol amounted to 67.5 p.c. It dissolved in 3 vol. of 70 p.c. alcohol and became opalescent on addition of 10 vol. The odour was excellent[1]).

Peppermint Oil, Russian. From an English contemporary[2]) we cull a few notes on peppermint cultivation in Ukraine. Formerly the oil produced in that country was chiefly used in the local tobacco industry, but the yearly production has become bigger. It now amounts to about 20000 lbs. of peppermint and 1000 lbs. of spearmint oils, so that the distillers find themselves compelled to sell part of their output abroad. The properties of Ukraine peppermint oil are as follows: d 0.904; α_D — 26°; total menthol 53.8 p.c.; ester (calculated as menthyl acetate) 6.0 p.c.; soluble in 3 vol. of 70 p.c. alcohol, upon addition of 10 vol. the solution becomes slightly opalescent.

Petitgrain Oil. According to an abstract from the *Review of River Plate*[3]), the export of petitgrain oil from Paraguay amounted to 71322 lbs. in 1913, against 52704 lbs. in 1912. This quantity was distributed as follows amongst the principal consuming countries: —

France	23400 lbs.
Argentine	25743 „
Italy	8378 „
Austria-Hungary	7430 „
Germany	5137 „

These figures, needless to say, do not give a correct idea of the consumption of the oil in the various countries, many of which receive the oil in transit only. Thus it is assumed that in the figure mentioned for Argentine, 16821 lbs. are included which were proved to have been sent to the United States. By the way, petitgrain oil is the only product exported to the United States from the Consular District of Asuncion.

Rose Oil, Bulgarian. It is not to be wondered at that prices for rose oil, which had reached nearly ℳ 3000.— per kilo (approximately 83/- per oz.), before the war could not be maintained at this level. It is but natural that the consumption

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[1]) *Perfum. Record* **6** (1915), 3. — [2]) *Perfum. Record* **5** (1914), 314. — [3]) *Commerce Reports* **1915**, 114.

of such an article is affected more particularly by the disturbances and upheavals of warlike times, as the oil is used exclusively in the manufacture of *articles de luxe*. Under the pressure of stagnant demand and the necessity to realize existing stocks as far as possible, prices shrank to about ℳ 900.— per kilo (= abt. 25/- oz.) in the course of the autumn 1914 and experienced a further drop in the early spring of this year, when it was found that there were still considerable parcels of good quality left unsold. In consequence of the cold weather, distillation only began in May this year, and was carried out under favourable conditions, as the rose plants had stood the winter well and but little damage by frost was noticed. The yield of the distillation is claimed to have been particularly abundant in the Karlovo district, having exceeded last year's result by about one fifth; on the other hand it is said that in the Kazanlik and other districts the quantity of oil obtained did not reach last year's output. Generally speaking the crop may be called a fair average one. That the position of the producers is not enviable this year in view of the general business stagnation, and that still further great sacrifices will be necessary before the receding tendency of the market has been brought to a standstill, goes without saying. The advent of peaceful times only will bring better conditions for those interested in the rose oil industry.

Statistical material from divers sources about the 1915 crop are before us, but as is usual the various statements differ so much one from another that neither of them can lay claim to absolute reliability. We only publish, therefore, the report of the German Consulate in Sofia which, at any rate, can be looked upon as absolutely impartial. The rose crop, so the report tells us[1]), and the distillation of the blossoms in Bulgaria began towards the end of May and lasted down to the beginning of July. Generally speaking the result was satisfactory. In the Stara-Zagora district an average of 200 kilos of red and 250 kilos of white rose petals were obtained for every 10 ares under cultivation, in the Kazanlik district the average yield amounted 150 kilos. The blossoms were a little less rich in oil than in the preceding year. One muskal (equal to about 1/6 oz.) of oil was obtained on an average from 18 kilos of flowers in the Kazanlik district, and from 12 to 13 kilos in Stara-Zagora. According to official records the total yield of this year's crop was as under in the various districts:—

district	rose fields (10 a.)	average yield of flowers	yield of rose oil muskals
Karlovo	31 896.8	4 784 520	281 442
Philippople	9 499.8	1 899 860	118 741
Peshtira	2 028.2	456 310	38 025
Panagurichté	450	112 500	7 031
Pazardjik	73.2	14 640	915
Stara-Zagora	38 529.1	830 000	64 000
Kazanlik	—	—	300 000

Thus the total production amounted to about 810154 muskals or 3888 kilos.

P. Siedler[2]) reports on the properties of a rose oil which had been sent to him from Bulgaria as guaranteed pure. The oil was clear and of a yellowish colour. The first crystals began to form at 22°. The crystallization-point[3]) is therefore 22°. For

[1]) *Nachr. f. Hand., Ind. u. Landw.* **1915**, No. 75, p. 5. — [2]) *Pharm. Ztg.* **60** (1915), 179. — [3]) Comp. *Report* April **1913**, 90; footnote.

comparison purposes a sample of palmarosa oil was used, such oils being, as is well known, often resorted to for adulteration of rose oil. It was also clear and of yellowish colour.

The rose oil had the following constants: d_{240} 0.8565; acid v. 2.93; ester v. 7.06; iodine value 169.06 and the palmarosa oil: d_{240} 0.8925; acid v. 1.13; ester v. 17.71; iodine value 215.01.

As Siedler had reason to suppose that the composition of Bulgarian rose oil differs, according to the place of production and to the quantitative proportion of red and white rose petals used in its production, he refrained from drawing any conclusions from the above-mentioned figures.

F. Dietze [1]) now reverts to Siedler's work, and as the values found confirm his own former observations, he gives Siedler's results once again, along with the constants of the most generally used adulterant, and with his own figures laid down 18 years ago. d_{270} rose oil Siedler 0.8545, Dietze 0.845 to 0.866; palmarosa oil Siedler 0.891. Crystallization-point rose oil Siedler 22°, Dietze not below 15°; sap. v. rose oil Siedler 9.99, Dietze not above 10; palmarosa oil Siedler 20.64; ester v. rose oil Siedler 7.06, Dietze 6.5 to 8; palmarosa oil Siedler 17.71. Ratio (calculated on acid and ester values) rose oil Siedler 3.41; Dietze not above 7; palmarosa oil Siedler 15.7.

J. Mendel [2]) writes on the economic importance of rose oil. He discusses chiefly the conditions of production, the industry and the distilleries. He reports in the form of tables on the crops in the various Bulgarian districts from 1891 to 1913, as well as on the export of rose oil and rose-water from Bulgaria. Our own rose production in Miltitz is also given a short paragraph.

Rose Oil, French. R. M. Gattefossé [3]) reports on rose oils obtained in the South of France from cultivated roses. The "rose Brunner" ("Ulrich Brunner rose") furnishes an oil melting above 28°, the yield being 1 kilo from 18000 to 20000 kilos of blossoms. The oil from the roses "Louis van Houtte" and "Marie van Houtte" is distinctly green when freshly distilled, but it soon assumes the pale yellow colour of the Bulgarian oil; m. p. 16°; α_D — 11°; sap. v. 9.8. Furthermore mixtures of various well known species of roses had been distilled which yielded a product of good odour: d 0.864; α_D — 2.2°; sap. v. 32; m. p. above 26°.

The rose "Ulrich Brunner" seems to be particularly well suited for the production of rose-water, more especially so when mixed with *„rose de mai"*.

The *"rose de mai"* is generally used in the South of France for the manufacture of rose-water. The yield is bad: 10000 to 110000 kilos of roses furnish 1 kilo of oil and 10000 litres of rose-water. According to Gattefossé the cause is to be found in the fact that the roses are often exposed for hours to carriage by rail. They may only reach the factories towards noon, and it often happens that they cannot be distilled till next day. Moreover, the stills used in Grasse, which are supplied with a "swan's neck", are not suitable for the work. In La Colle the flower farmers have obtained results as satisfactory as in Bulgaria in their modernly equipped distillery. The stills hold from 1000 to 1500 kilos of flowers; neck and head are short and wide.

We may here add that the above-mentioned low yields are explained by the fact that in the South of France the roses are mainly worked for rose-water, the oil being

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[1]) *Südd. Apotheker Ztg.* **1915**, 57; *Pharm. Ztg.* **60** (1915), 331. — [2]) *Deutsch. Parf. Ztg.* **1** (1915), 54. — [3]) *Perfum. Record* **5** (1914), 316.

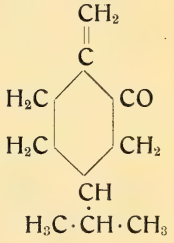
obtained as a by-product only. Little importance need be attached to the melting point of rose oil, for by altering the process of distillation it is possible to produce rose oils of different melting points.

According to Revillet[1]) the labourers engaged in the rose crop at the Riviera suffer from diseases of the skin of their hands every winter. Some of the symptoms are of an eczema-like nature and are produced by the various insecticides used in the rose plantations. Others are the result of infection by horse manure which is chiefly used by the growers. Finally the hands may get injured by coming in contact with the thorns, or small thorns may be left embedded in the skin. These often cause suppuration, especially with beginners; labourers who have worked in the rose fields for some years appear to acquire a certain amount of immunity. Revillet has never observed cases of tetanus, but a few cases of botryomycosis which have most likely to be attributed to infection by horse manure. Revillet advises the workmen to wash their hands well after their work is done, and to remove all the thorns that may have penetrated the skin; wounds or abrasions should be treated with tincture of iodine.

Santolina Oil. On page 41 of our previous *Report* we pointed out that according to L. Francesconi and N. Granata α-santolinenone is a racemic body, the hydroxylamino-oxime of which may be split into the optical antipodes by means of *d*-camphor sulphonic acid. Though the separation has not been completed so far, the authors, in collaboration with A. Sanna[2]) have now published a few particulars. The *d*-camphor sulphonate of the *l*-hydroxylamino-oxime of α-santolinenone melts at 192 to 196°; $[\alpha]_D$ — 20.35°. The *l*-hydroxylamino-oxime of the α-santolinenone melts at 171°; $[\alpha]_D$ — 115.7°.

Similar results were obtained with *d*-bromocamphor sulphonic acid.

Francesconi and Granata[3]) consider a closer examination of the hydroxylamino-oxime as being of special interest for the elucidation of the structure of α-santolinenone. When treating this compound with dilute acids, the expected ketone was not obtained; the hydroxylamino-oxime behaves in a manner analogous to pulegone hydroxylamino-oxime (compare page 82 of this *Report*). From the abnormal refraction values and from the behaviour of the hydroxylamino derivatives in comparison with those from pulegone the authors deduce the correctness of the constitution formula adopted by them for α-santolinenone.



α-Santolinenone.

When heating α-santolinenone hydroxylamino-oxime in alcoholic solution, α-santolinenone amino-oxime (m. p. 155°) and α-santolinenone dioxime (m. p. 260°) were formed. When boiling the hydroxylamino-oxime with alcohol and mercuric oxide, a larger yield of dioxime is obtained. On continued boiling with dilute hydrochloric acid, α-santolinonene hydroxylamino-oxime forms a compound $C_{10}H_{16}N_2$ (a nitrilimine?) of the m. p. 119 to 120° and α-santolinenone imino-oxime (m. p. 169 to 172°). The latter compound is not always produced. It happens occasionally that in its place α-santolinenone imine is obtained.

Solidago Oil. The great Compositae genus of *Solidago* is represented in the United States by no less than 75 species, very few of which have been treated phytochemically.

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[1]) *Lyon Medical; Répertoire* **26** (1914), 360; *Pharmaceutical Journ.* **94** (1915), 287. — [2]) *Gazz. chim. ital.* **44** (1914), II. 354; *Chem. Zentralbl.* **1915**, I. 788. — [3]) *Gazz. chim. ital.* **45** (1915), I. 167; *Chem. Zentralbl.* **1915**, I. 1313.

So far the oils from *Solidago canadensis*, L., *nemoralis*, Ait., *odora*, Ait. and *rugosa*, Mill.[1]) have been described. The oils of the two last-named kinds have now been examined more closely by E. R. Miller and J. M. Moseley[2]).

Solidago rugosa is found in damp thickets, and on the borders of fields, from Newfoundland to Ontario and south-westward to the Gulf of Mexico. The fresh herb yielded 0.4 p.c. of essential oil ($d^{25°}_{25°}$ 0.8620; α_D — 12° 8′; $n_{D20°}$ 1.4813; sap. value 4.22; sap. value after acet. 10.97) which boiled between 165 and 180° and appeared to consist chiefly of *l*-α-pinene, the properties and the formation of a nitrosochloride pointing that way. The constants of the higher-boiling parts seemed to indicate that *d*-limonene and β-pinene may also have to be considered as constituents of the oil.

Solidago odora, commonly known as Sweet Scented Golden-rod or Blue Mountain Tea, grows on dry or sandy soil on the borders of thickets and in open woods, from New Hampshire to Florida and westward to Missouri and Texas. The authors presume that the golden rod oils met with in commerce for many years were probably nothing more than nondescript oils distilled from a mixture of weeds without any attempt at selection. In their distillation experiments the authors obtained yields averaging about 1 p.c.; the lowest was 0.64, the highest (in one instance) 1.53 p.c. The odour of the oil was somewhat like that of anise, and at the same time suggestive of safrole. $d^{25°}_{25°}$ 0.9310; α_D + 13° 72′; $n_{D28°}$ 1.5065; acid v. 0.63; sap. number 7.9. Methylchavicol was proved by oxidation to anisic acid (m.p. 184°) and homoanisic acid (m.p. 85 to 86°). The content of methylchavicol amounted to about 76 p.c. (methoxyl determination). Anethole was not present; phenols, aldehydes and ketones were also absent. The presence of α-pinene is doubtful; although the hydrocarbon furnished a nitrosochloride of the m. p. 103°, it had no properly melting nitrolamine bases. Phellandrene reaction was negative, and camphor could not be proved. On the other hand borneol was characterized by its melting point (203 to 204°) and phenylurethane (m. p. 138 to 139°). Besides borneol another alcohol appears to occur in the oil. In the saponification lyes there were present presumably three volatile acids and a non-volatile one.

The oil obtained from cultivated plants showed properties similar to the oil from wild herb. $d_{25°}$ 0.9450; α_D + 9.33°; $n_{D24°}$ 1.5140; sap. v. 8.9; sap. v. after acet. 19.4; soluble in 0.4 vol. of 90 p.c. alcohol; upon addition of 15 volumes, the solution became opalescent.

Spearmint Oil. The use of this oil in the American chewing gum and confectionery industry, which we had always looked upon as an aberration of taste, has, according to a report of our New York friends, declined to such an extent that the oil is threatened with complete depreciation. The quantities grown in the West exceed the present requirements so much that large parcels are lying about everywhere unsold and cannot be placed even at considerable sacrifices. In February 1914, spearmint oil cost $ 3.80 per lb. in the U. S., whereas now the best oil may be had at $ 1.40 to $ 1.50 per lb. at most. It is, of course, difficult to say whether the great European war has anything to do with this considerable drop in prices; the export of the oil to Europe has never been very important.

In a price-list, E. M. Holmes[3]) found an oil styled *"Oleum Menthae Sativae* B. P." whereby spearmint oil was meant. The designation of *"Oleum Menthae Sativae"* occurs last in the London Pharmacopoeia for 1788, but was changed to *"Oleum Menthae*

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[1]) Comp. Gildemeister and Hoffmann, *The Volatile Oils* 1st ed., p. 668. *Report* April **1906**, 62; October **1906**, 72; April **1915**, 43. — [2]) *Journ. Americ. Chem. Soc.* **37** (1915), 1285. — [3]) *Pharmaceutical Journ.* **94** (1915), 229.

viridis" in 1809. The *Index Kewensis* distinguishes between three different kinds of *Mentha sativa*, i.e. *M. sativa*, L., which is the original type, *M. sativa*, Roxb. = *M. arvensis*, L. var. and *M. sativa*, Sm. = *M. aquatica*, L. var. No oil has been distilled so far from either of these mints.

Thyme Oil. In Limaru (British East Africa) thyme oil was distilled some little time back[1]). The plants had been raised from English and French seeds.

The oil distilled from English thyme (yield 0.5 and 0.7 p.c.; d 0.901 and 0.905; n_D 1.4900 and 1.4768) contained 32 p.c. of liquid phenols, the one from French thyme (yield 0.38 p.c., d 0.905; n_D 1.4908) 40 p.c. of readily crystallizing phenols.

Turpentine Oil. The possibility has been discussed repeatedly of late to create a home resin industry in Germany, in order to render the country independant of American and French turpentine products[2]). The prospects for the creation of turpentine manufacture in Germany seem to be fairly favourable, for, according to the statement of an Austrian expert who had been asked by the Prussian Government to examine the State Forests of "Prussian Poland" (province of Posen) from the point of view of resin production, these woods should produce a crop of resin and turpentine oil worth more than two million marks annually. To this would have to be added the numerous great private forests which would undoubtedly fall in line with the Government. If further examinations of other Prussian State forests produce similar results, the yield of the Prussian forests alone would cover about half the requirements of Germany. If the remainder of Germany joins in the movement, the whole requirements could be covered in this manner. Needless to say, some time will have to elapse before this can materialize.

According to a report in the *Chemiker-Zeitung*[3]), the tendency of the American market was very depressed down to the middle of September. Prices had reached a low level, which had been simply regarded as utterly impossible amongst producers. Even a reduction in the production could not stop the crumbling away of prices, although it had been carried out on a fairly liberal scale. In the four principal markets, Savannah, Jacksonville, Pensacola and Brunswick, the short production in turpentine oil amounted to 15000 barrels in round figures in July this year, and to about 40000 barrels of rosin. This amounts to a reduction in July by about 25 p.c., and even 32 to 33 p.c. when the period from the beginning of April to the end of June is considered. However, even this important reduction did not prevent prices from dwindling temporarily to 38 cents in New York and 35 3/8 cents in Savannah. In consequence of the new Inspection Law in Florida, the possibility of joint selling operation is out of the question. Every attempt in this direction on the part of the producers failed so far. These fruitless endeavours have induced the southern States to draw the American Government's attention to the supply, by the northern States, of war material for England and France, which prolongs the war and which would seriously damage the southern States as long as the war lasted, apart from the heavy losses already sustained. The stand taken by the southern States against the northern States has assumed the form of an open fight, but as America (i.e. the Washington Government) is not inclined to use determined language in London as regards permission of unhindered export of

[1]) *Perfum. Record* **5** (1914), 423. — [2]) *Seifenfabrikant* **35** (1915), 617, 645. — R. Bürstenbinder, *Deutsche Parf.-Ztg.* **1** (1915), 81. — W. Rojahn, *ibidem* 139. — [3]) *Chem. Ztg.* **39** (1915), 768.

turpentine oil to Europe, all efforts on the part of the southern States will be in vain. In the long run the reduction in production is bound to raise prices to their old level, the more so as the quiet summer trade is now past. On the New York Exchange prices have reached 41½ cents a gallon in the course of a fortnight, and in Savannah 38½ cents. But no illusions are entertained in the American markets and no improvement of the unsatisfactory state of the naval stores industry need be looked for as long as the war lasts.

A new Law regulating the trade of turpentine and rosin has been promulgated in Florida[1]). The chief point laid down is that the sale of turpentine is only permitted in vessels on which the nature of the contents is distinctly marked. At the same time the designation "spirits of turpentine" shall only be applied to the pure and unadulterated oil distilled from "gum" or "scrape" of the pine-tree, and the designation of "wood spirits of turpentine" to all other oils or distillates resembling spirits of turpentine, or being used as a substitute, and obtained in a direct or indirect manner by distillation of the wood or any raw material other than pine resin (gum). If these two articles are adulterated or mixed with any other ingredient, they are to be labelled "adulterated". Contraventions are punished with a fine of $ 1000.—, or imprisonment not exceeding one year, or both, at the discretion of the Court. Even the purchase of improperly labelled turpentine will be punished. "Rosin" must not be packed together with any other article than pure pine-tree rosin, and it should not be packed in such a way as to make it appear as though the vessel contained a better grade than is really contained in it. As regards classification, the standard types, as laid down by the Department of Agriculture in Washington, shall be used[2]). By the signature of the State Governor this Law came in force on the 10th of June.

Turpentine oil from Pinus clausa. A short pine occurs in Florida, *Pinus clausa*, Sarg *(Coniferae)* which is called sand pine. Its turpentine yields 18.93 p. c. of volatile oil on which Schorger has published a report[3]). $d_{15°}$ 0.8724; $\alpha_{D20°}$ — 22.65°; $n_{D15°}$ 1.4768. It contains 10 p. c. of *l*-α-pinene (nitrolpiperidide, m. p. 119°), 10 p. c. of *l*-camphene (conversion to *iso*borneol, m. p. 207 to 209°) and 75 p. c. *l*-β-pinene (nopinone semicarbazone, m. p. 189°). The *l*-β-pinene is readily isolated from this oil in the pure state.

D. E. Tsakalotos[4]) describes the properties of two authentic samples of Greek turpentine oil from *Pinus halepensis*, Mill. They consisted almost entirely of *d*-α-pinene. The properties of these oils, distilled in 1907 and 1914 respectively, were as follows: b. p. 155 to 156°; $d_{25°}$ 0.8545 and 0.8543 to 0.8546; $[\alpha]_D$ + 47.9 and + 46.8 to 47.2°; $n_{D25°}$ 1.4635 and 1.4636 to 1.4638.

On page 81 of the second volume of the work *Die ätherischen Öle* (2nd ed. by E. Gildemeister), the origin and manufacture of Russian turpentine oil has been amply described. A further contribution to the subject is found in the report of the *Russische Technische Gesellschaft* for 1914, in which A. Kind describes turpentine oil manufacture in Russia[5]). He distinguishes between two processes: 1. distillation by steam of the product of tapping pine tree trunks. The distillate is called Sierny turpentine oil or essential turpentine oil. 2. Dry distillation of the wood in furnaces; the raw material

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[1]) *Zeitschr. f. angew. Chem.* **28** (1915), III. 469. — [2]) Comp. *ibidem* 341, 417. — [3]) *Journ. Ind. Eng. Chemistry* **7** (1915), 321. — [4]) *Journ. de Pharm. et Chim.* VII. **11** (1915). After a reprint kindly placed at our disposal. — [5]) Oil and Colour Trades Journal of the 10th and 15th of April, 1915; *Farbenztg.* After *Seifensieder Ztg.* **42** (1915), 645.

consists of old pine stumps or parts of pine tree trunks, also of pine trees which have been tapped "dead". This distillate is called resinous essential turpentine oil, furnace turpentine oil, stump or block tar.

In the manufacture of turpentine oil four principal districts have to be considered. The northern region comprises the governments of Archangelsk and Vologda, especially between the river-courses of the Vaga and the northern Dvina. Here but little Sierny turpentine oil, but chiefly furnace turpentine oil is obtained. The production in the Vaga districts is estimated at about 100 000 poods (1 pood = 36 lbs.) of turpentine oil, which is produced mostly in small distilleries (home industry) by about 10 000 people. The north-eastern region includes the governments of Viatka and Perm, where along the navigable rivers and the railway lines much turpentine oil is produced in small private distilleries; about 3500 people are said to be occupied in this work. The central region includes the governments of Vladimir, Kasan, Kostroma and Nishni-Novgorod; medium-sized concerns are working the State as well as private forests, especially along the course of the river Volga. In Kasan it is said that about 2500 people are engaged in turpentine oil manufacture. In the north-western region, Kind includes the governments of Vilna, Vitebsk, Volhynia, Grodno, Kovno, Minsk and Mohilev. Here turpentine oil is produced in private forests, chiefly along the railway lines, less so along the banks of the river Niemen. The district Borissov in the government of Minsk is said to produce about 300 000 poods annually. Besides these principal districts there are other governments in Russia which take part, though in a minor degree, in the turpentine oil production. In the Caucasus, in Siberia and in Poland a little is obtained. In Finland, however, the industry is but little developed. The total production of turpentine oil in the Russian Empire is estimated at about 1½ million poods annually, of which about 800 000 poods are exported.

In the production of turpentine oil[1]) by dry distillation, iron vessels are used. A charge amounts to 2 to 2½ cubic arshin (1 arshin = abt. 28 inches), the yield being from 3 to 4 poods of a reddish oil of inferior quality from 1 cubic sashen (abt. 10¾ cubic yards) of raw material. The Vologod still produces somewhat better results. Its capacity is from ¼ to ¾ cubic sashen, the yield being 3½ to 7 poods. This still is almost exclusively used in the North, as well as in Siberia. An improved form with internal boiler is largely used in the northern Dvina district. The Viatka still furnishes a product containing a considerable amount of tar, the loss being about 60 p.c. upon rectification. The rectified oil is of dark colour and bad smell. The still holds ⅛ to ¼ cubic sashen, yielding about 12 to 14 poods. In the north-western region the cylindrical still of 1 cubic sashen capacity is used, the yield being about 12 poods. It produces a somewhat better turpentine oil than the first-named construction. A good product is obtained with the Sushilky still, the so-called dry still, which is met with in the southern region (government of Viatka). It holds 1½ cubic sashen and supplies about 12 poods of rectified oil. With a still worked in the southern districts of Viatka, and which represents a combination of the north-western with the Sushilky still, an excellent turpentine oil is produced. It shows a laevo-rotation of 26 to 30°, contains considerable quantities of low-boiling parts, does not smell unpleasantly after repeated rectification and is colourless.

The author examined more than 50 Russian turpentine oils of different ways of manufacture and points out that it is erroneous to suppose no good oil could be

[1]) The designation "turpentine oil" for a product obtained by dry distillation must be avoided; it can here be a case of "pine tar oil" only.

produced by means of dry distillation[1]). If this distillation is properly conducted and if the construction of the plant, technically speaking, is adapted to the raw material, the oil obtained will suffice to the requirements of the industry as well as pharmacopoeias. It is admitted, however, that a thorough alteration in the production of turpentine oil would still have to be carried out in Russia.

For the trade in Russian turpentine oil, the north-western region is important. There is no home industry there, and all the firms engaged in the manufacture are well founded. The obstacles in the way of the development of Russian turpentine oil production are the small private distilling plants (home work) amounting to more than 20000 plants which are mostly in the hands of merchants.

A. Madinaveitia[2]) has oxidized rectified Spanish turpentine oil of the b. p. 155 to 156° with permanganate after the directions of Wallach. The volatile parts having been eliminated by distillation with steam, oxalic acid and 1.5 p.c. of sodium nopinate were obtained from the aqueous solution. As Wallach speaks of a yield of 5 p.c., Madinaveitia presumes that Spanish turpentine oil contains less β-pinene than French or American oil.

Concerning the desinfecting properties of turpentine oil, see page 71 of this *Report*.

The use of pinene ozonide in the treatment of pulmonary tuberculosis is discussed on page 71 of this *Report*.

Vetiver Oil. From various samples of Indian vetiver root, Puran Singh[3]) obtained from 0.37 to 1.14 p.c. of oil. According to his indications, roots of good condition and quality should yield from 0.7 to 1 p.c. of oil. Lower yields point to bad quality of the raw material. The best time for collecting the roots is towards the end of January; during the rainy season the roots contain but little oil.

In the oil rectified by steam distillation, the author found the following constants: $d_{15°}$ 1.011; α_D — 30.65°; $n_{D20°}$ 1.5165; acid v. 10.5; ester v. 69.6; sap. v. after acet. 132.8; soluble in 80 p.c. alcohol. The resin left in the flask had the following properties: $d_{30°}$ 1.132; α_D + 488.04°; acid v. 46.92; ester v. 64.28.

So far dextro-rotation had always been observed with vetiver oil, but the above-described rectified oil showed laevo-rotation. The author presumes that dextro-rotation is caused by the presence of resin in the unrectified oils. This supposition sounds rather strange and induced us to rectify by steam distillation an oil produced by ourselves from finest selected raw material. As was suspected by us from the very beginning, the observation made by Singh was not confirmed by our experiment. The original oil showed + 23° 25′, and the rectified oil + 17° 40′, the residue having a rotation of + 28° 42′. Even a distillation carried out under atmospheric pressure over the naked fire, a process in the course of which decomposition might, under certain conditions, result in an alteration of the rotation, yielded only dextro-rotatory fractions. The first 50 p.c. rotated + 20°, and further 25 p.c. + 12° 20′. The optical behaviour of the residue could not be determined, as the major part of it had become carbonized. Thus an explanation of Singh's statements is impossible, the more so as they are

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[1]) We are of opinion that it is impossible to obtain an oil of the properties of turpentine oil by dry distillation. It is a pity that the author gives no indications as to constants and composition of the oils examined by him. — [2]) *Ann. Soc. Esp. Ph. Ch.* **12** (1914), 259; *Bull. Soc. chim.* IV. **16** (1914), 785. — [3]) *Chemist and Druggist* **85** (1914), 225. — *Americ. Perfumer* **10** (1915), 133.

difficult to check, seeing that the author has not given the slightest indications as to the properties of the original oil.

Wintergreen Oil. In our *Report* of April **1914** (page 98) we mentioned a colour test published in the *Perfumery and Essential Oil Record* for distinguishing natural from artificial wintergreen oil. The test is carried out as follows: 5 drops of the oil to be tested are mixed with 5 drops of a 5 p.c. alcoholic vanillin solution and 1 cc. of alcohol, and well shaken. Next 2 cc. of concentrated sulphuric acid are added, and the mixture is again well shaken. Natural oil produces an intense crimson colour, while artificial oil yields a yellow colour.

Since then a few further colour reactions have been recommended for the same purpose by G. N. Watson and L. E. Sayre[1]). In one of the tests the oils are mixed with an excess of sulphuric acid. It is claimed that gaultheria oil will produce an intensely red, birch bark oil a yellowish or faintly red, and artificial methyl salicylate no colouring at all. A second test consists in a few drops of the oil to be tested being mixed with 2 cc. of concentrated sulphuric acid and 2 drops of a saturated alcoholic solution of heliotropin. In this case gaultheria oil will cause a pronounced red colour, which, upon addition of alcohol, is converted into a dark violet colour. In the case of birch bark oil the colour shades are similar but somewhat less pronounced, whereas the artificial product yields a yellow colour, which, however, is to be attributed solely to the influence of sulphuric acid on heliotropin. The following is recommended as a still better test, capable above all of distinguishing between gaultheria and birch bark oil: 1 cc. of the oil is mixed with 2 cc. of concentrated sulphuric acid, 1 cc. of a saturated aqueous solution of chloralhydrate being added. It is claimed that with this test gaultheria oil will develop a dark green coloration, the dark green oily layer showing above a lighter green aqueous zone. This becomes more pronounced when 2 to 3 cc. of water are added. Birch bark oil yields a dark violet oil layer, whereas methyl salicylate affords no coloration at all, or else a faint violet shade which becomes noticeable only after prolonged standing.

In connection with these reactions a well known means of distinction between natural and artificial oil is called to mind. The natural oil, on being shaken, shows a slight froth at the top which lasts for a short while, the artificial oil, however, shows no froth at all. It is also claimed that a rise in the temperature, when mixed with sulphuric acid, only occurs in the case of natural oils. This contention, however, is not correct, as we have ascertained ourselves and as was to be expected.

Opinions as to the value of the tests recommended by Watson and Sayre may differ. Apart from the fact that colour reactions are always a make-shift of doubtful value, above-mentioned tests, as we had occasion to convince ourselves in guaranteed pure oils distilled by ourselvess, can only be used for distinguishing between natural and artificial oil at most. When tried with gaultheria or betula oil, the reagents produced either identical results, or else the differences were so slight as to permit of no conclusions whatsoever. Generally speaking it could be established that the colour shades were a little more pronounced with gaultheria oil than with betula oil, but we failed to observe positive differences in the colouring, not even with the chloralhydrate test, where we waited in vain for the green colouring of gaultheria oil. In this case both natural oils showed brown coloration, which was converted into a turbid violet when water was added. Artificial oil remains colourless in this reaction,

[1]) *Journ. Amer. Pharm. Assoc.* December **1914**, 1, 658; *Pharmaceutical Journ.* **94** (1915), 281.

but the mixture with concentrated sulphuric acid assumed a light yellow shade. We consider the use of heliotropin a failure, for it offers no advantage over the ordinary sulphuric acid test. The violet coloration observed upon the addition of alcohol, and which Watson and Sayre consider as being specially characteristic for gaultheria oil, is of no importance whatsoever, for it shows itself as soon as sulphuric acid is brought in contact with heliotropin solution.

We repeat it, these colour reactions may possibly be found useful for distinguishing natural wintergreen oil from the artificial product, which is certainly of some use. But as soon as one has to deal with mixtures of both oils, these tests will fail in most cases, seeing that colour shades would have to be depended upon from which definite conclusions could only be drawn in exceptional cases. To show what value is attached to these colour tests in other directions, we refer to a remark made by H. Gesell[1]) in a criticism concerning the same subject. He believes that it would be easy to add substances to the artificial methyl salicylate which would not betray their presence by their odour, and which would yet produce the coloration characteristic for the natural oil. For, as he ascertained by experiments, the natural ester, when isolated from the oils in its pure form, behaved in exactly the same way as did the artificial ester in the presence of the various reagents, thus proving that the colouring is due to secondary constituents.

Wormseed Oil, American. This oil appears to maintain its predominating position on the list of the numerous vermifuges. In 1913 a brisk demand in the following year had been anticipated and the producers in Carrol county, Maryland, as well as the middlemen in New York had considerable stocks at their disposal. Exports, however, to the belligerent countries being conspicuous by their absence, brought great disappointment to all interested parties and in the course of last year prices receded from $ 1.85 to $ 1.35. It was only in May this year that the oil began to attract a little more, though partly speculative attention and once again to reach a price level which left a margin of profit to the producers. The last price quoted by New York was $ 2.— per lb. Unfortunately no statistical data are available as to the extent of the 1914 and 1915 crops.

In the course of the last few months two samples of oil were submitted to our laboratories for examination. Both had been offered to our customers as American wormseed oil, but in reality they had but the name in common with this article. To judge from the odour which did not remind in the least little degree of wormseed oil, we had to deal with mixtures of eucalyptus and anise oil. Unfortunately in both instances but very small samples had been placed at our disposal, so that we had to confine ourselves to the determination of specific gravity and optical rotation, points from which, however, no conclusions could be drawn in either case as regards quality of the oil. We refrain, therefore, from mentioning the values ascertained, suffice it to have pointed out these "substitutes", so as to put buyers of American wormseed oil on their guard.

In our *Report* October **1913**, page 107, we communicated particulars about an adulteration with cineol, observed by us some time previously.

Experimental examinations concerning the poisoning properties of American wormseed oil (chenopodium oil) have been carried out by W. Salant and E. K. Nelson[2]).

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[1]) *Americ. Perfumer* **10** (1915), 33. — [2]) *Amer. Journ. Physiol.* **36** (1915), 440; *Chem. Zentralbl.* **1915**, II. 36.

With cats and dogs the oil produces symptoms of depression of the higher nerve centres; later on convulsions follow. With dogs, rabbits and guinea pigs, the power of resistance against chenopodium oil is about the same, for the cat the drug seems to be more poisonous. Internal administration requires about double the dose used in subcutaneous injections; ascaridol is more than 30 p. c. more poisonous than chenopodium oil.

Ocker[1]) describes the fatal case of a boy who died within 5 days after taking 31 drops of American wormseed oil, and believes to be justified in putting down the fatal issue to poisoning by wormseed oil.

Wormwood Oil. It is not surprising to note that the sale of all kinds of wormwood oils left much to be desired these last few years, seeing that the chances of consumption have been greatly circumscribed by the stringent absinth laws introduced by most of the European States. American wormwood oil, of which there is no lack of supply, cost $ 4.25 per lb. in February 1914, whereas to-day it is difficult to realize $ 2.25 in the producing districts. The great reputation of wormwood oil of our own drawing from herb cultivated by ourselves in Miltitz, has added to the fact that the demand for the American oil has become smaller little by little. Our own plantations look very well and promise excellent results.

Cultivation and distillation of wormwood in Wisconsin have been described by R. H. Denniston and R. E. Kremers[2]). Formerly the oil distilled along the Atlantic border was looked upon as unfit for use until shipped to Europe, whence it was re-imported as "European oil". Later it was thought that the climate of the western United States had an unfavourable influence on the oil produced in these states. To-day, however, a fair amount of wormwood is cultivated in Wisconsin, though almost exclusively in Sauk County. The immediate financial advantages derived from wormwood cultivation are not great, but its importance lies in the fact that it is an additional element in diversified farming. The crop alternation usually practised in Wisconsin is as follows: wormwood, maize, oats or barley, wormwood. The rotation, however, is not a three-year rotation, since wormwood is allowed to stand longer than one season. Wormwood sown the first year, with oats or barley as a cover crop, can only be harvested in the second year, the yield in oil being then greatest. It is continued until the oil yield becomes too low to render distillation profitable. Maize is then planted, the cultivation of which puts the soil in good condition. After this follow oats or barley, wormwood being sown at the same time. Cultivation in rows is very favourable for the development of the wormwood plants. But this method is not practised in Wisconsin for two reasons: First, the acreage is usually too vast to permit of transplanting by hand, and, secondly, the wormwood fields are used to pasture cattle. The cattle does not touch wormwood. The fields can be used as pasture until about a fortnight before the beginning of distillation, unless the cattle is molested too intensely by flies.

Wormwood seed is almost microscopically small. Before sowing, the soil must be well prepared. It is claimed that no harrowing should be done after sowing, as the first rains will cover up the seed sufficiently with soil.

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[1]) *Zeitschr. f. Med.-Beamte* **1915**, N° 3; *Pharm. Ztg.* **60** (1915), 206. — [2]) *Bull. Univ. Wisconsin*, Serial N° 738. Gen. Ser. N° 542, Madison 1914, p. 32.

Wormwood herb is richest in oil when in full florescence. The herb is cut the day before distillation, so that it reaches the still somewhat wilted. Aromatic weeds, such as *Erigeron canadensis* and *Ambrosia artemisiaefolia*, should be carefully removed. Distillation of a charge usually lasts about ten hours. Little need be said about the distilling plant; the still itself mostly consists of a large wooden vat. Condensation is carried out by water, in some parts by water and air combined. The distillation water is discarded and the exhausted herb taken back to the fields, where it is eaten by the cattle. If eaten by milk cows, the milk is said to acquire a slightly bitter taste.

On page 45 of the same *Bulletin*, E. R. Miller has published a chemical study of Wisconsin wormwood oil [1]). He has found that the cultivation in rows yields a better herb and consequently a better oil than meadow cultivation. With six authentic wormwood oils distilled in Wisconsin, Miller established the following properties: $d\frac{25°}{25°}$ 0.9230 to 0.9364; $n_{D\,190}$ 1.4675 to 1.4725; soluble in 0.7 to 0.8 vol. of 80 p.c. alcohol; sap. v. 73.8 to 100.4; sap. v. after acet. 113.9 to 157.1.

Italian wormwood oil, obtained by V. Paolini and R. Lomonaco [2]) at the rate of 0.46 p.c. from herb grown in the neighbourhood of Rome, was a greenish-brown liquid of not unpleasant odour. It did not dissolve in 80 p.c. alcohol. The oil contained 10 p.c. α- and β-thujone (semicarbazone), about 48 p.c. of thujylalcohol (hydrogen phthalate), furthermore phellandrene (nitrosite, m. p. 105°) and cadinene (dihydrochloride). Thujylalcohol was present in the free state as well as esterified with acetic, *iso*valeric and palmitic acids. We have here to deal with a mixture of at least two different alcohols, among which δ-thujylalcohol predominates.

New Pharmacopoeias.

At the beginning of this year, new pharmacopoeias came into force in England as well as in Finland. We shall discuss these publications in the usual way, as far as articles of our industry come into consideration.

British Pharmacopoeia.

(The British Pharmacopoeia 1914.)

In view of the comprehensive preparations which had been undertaken in the compilation of the new British Pharmacopoeia, it was to be expected that contents and methods of examination would be in keeping with the requirements of modern times. As far as essential oils and kindred articles are concerned, this is the case generally speaking, for not only have directions been altered where necessary, but they have also been amplified. For instance: the rotation has now been taken into consideration throughout, the only exceptions being turpentine oil and, strange to say, clove oil. Furthermore with oils containing esters, alcohols, aldehydes and cineol, a quantitative determination of these constituents is required wherever these bodies are of importance to the quality of the respective oils, &c., &c. Special directions for the various determinations are given in a separate chapter. One innovation we cannot approve of,

[1]) See also *Bull. Univ. Wisconsin*, N° 693. — [2]) *Rend. della R. Accad. dei Lincei, Roma* (5), **23** (1914), II. 123; *Chem. Zentralbl.* **1915**, I. 607.

viz., the inclusion of the refractive index. Several years ago (*Report* April **1910**, 134), when discussing the suggestions made by Hill and Umney for the B. P., we stated that we did not consider it advisable to embody such a constant in a pharmacopoeia, seeing that its limits of value have not by any means been laid down with the required degree of accuracy, and seeing also that for the individual oil this value is, almost without exception, less characteristic than any of the other constants. Our opinion has not altered since then. The figures indicated can only be looked upon as approximate and the limits of value cannot be considered reliable. In part they differ considerably from our own observations. Yet, strange to say, this constant is looked for in vain with artificial wintergreen oil. As this is a uniform chemical body, indications as to refractive index would have been much more called for in this instance than with essential oils. In the discussion which now follows the refractive index is not touched upon any more, for obvious reasons.

Specific gravity and solubility are based on 15.5° C. This makes but little difference with specific gravity (about 0.0004 lower), as compared with usual temperature of 15°; but with solubility, which is usually observed at 20°, this must not be lost sight of. The requirements specified are of such a nature, however, that difficulties are not likely to ensue.

Among official oils, pine needle oil and pimento oil are not to be found any longer, on the other hand several oils have been admitted, as for instance ajowan oil, Siberian fir oil, lemongras oil, natural and artificial wintergreen oil; crude turpentine oil has been replaced by the rectified article.

We will now proceed to the discussion of the several articles.

Oil of Ajowan *(Oleum Ajowan)*. Colourless; $d_{15.5°}$ 0.910 to 0.930; α_D +1 to +2°[1]). Thymol content not below 40 p.c. (determined with 20 p.c. solution of sodium hydroxide).

[1]) The limits of value are not in keeping with facts. In oils of our own distillation we observed values between +0° 24′ and +5°.

Oil of Anise *(Oleum Anisi)*. The ordinary oil as well as star anise oil are official. Colourless or pale yellow; $d^{20°}_{15.5°}$ 0.975 to 0.990; α_D −2 to +1°; $n_{D25°}$ 1.552 to 1.558; soluble in 3 parts of 90 p.c. alcohol; congeals at about 15.5° and does not again liquefy below 17°. At least 80 p.c. boil between 225 and 235°.

Oil of Cade *(Oleum cadinum)*. Dark reddish-brown or nearly black; $d_{15.5°}$ about 0.990[1]); soluble in ether[2]) and in chloroform; partially soluble in cold, almost wholly soluble in hot alcohol of 90 p.c. strength; very slightly soluble in water, the filtered aqueous solution being almost colourless and acid to litmus; test for pine tar: 1 cc. of the oil is vigorously shaken with 15 cc. of petroleum spirit and filtered; to 10 cc. of the filtrate 10 cc. of a solution of copper acetate are added, the mixture is again well shaken and set aside until separation into two layers is complete; 5 cc. of the upper layer, when mixed with 10 cc. of ether, become pale brownish-yellow, but not green (absence of pine tar).

[1]) The specific gravity may exceed 1. Compare *Report* April **1909**, 58.

[2]) The solution mostly shows a flocculent deposit after a short time.

Oil of Cajuput *(Oleum Cajuputi)*. Green or bluish green; $d_{15.5°}$ 0.919 to 0.930; α_D not more than −4°; $n_{D25°}$ 1.460 to 1.467; cineol content not less than 45 p.c. (phosphoric acid method)[1]).

[1]) On previous occasions (*Report* April **1910**, 134), when discussing the suggestions made by Hill and Umney for the B. P., we gave vent to our surprise that such an unreliable method should be recommended for a pharmacopoeia. The fact of its having been adopted after all does not make it any better. We shall certainly not give any guarantees based on such a method of determination.

Camphor *(Camphora).* $d_{15.5°}$ about 0.995; m. p. about 175°; soluble in about 700 parts of water, in 1 part of 90 p.c. alcohol, in 0.25 parts of chloroform and in 4 parts of olive oil; very soluble in ether; burns readily with a bright smoky flame. It volatilises even at ordinary temperatures and sublimes without a residue when heated. It forms a liquid when triturated with chloral hydrate, menthol, phenol, thymol, &c.; a solution of 5 g. in sufficient 90 p.c. alcohol to produce 20 cc., exhibits at 15.5° an optical rotation of about + 10° (distinction from synthetic camphor).

Oil of Caraway *(Oleum Carui).* Colourless or pale yellow; $d_{15.5°}$ 0.910 to 0.920; α_D + 75 to + 82°[1]); $n_{D25°}$ 1.485 to 1.497; soluble in 1 part of 90 p.c. alcohol and in 10 parts of a mixture of equal volumes of 90 and of 70 p.c. alcohol; when fractionally distilled, not less than 50 p.c. distils above 200°.

[1]) We have repeatedly met with caraway oils of a gravity of 0.910, which rotated between 70 and 75°.

Oil of Chamomile *(Oleum Anthemidis).* Blue when freshly distilled, but gradually becoming greenish or brownish-yellow under the influence of light and air; $d_{15.5°}$ 0.905 to 0.915; α_D — 1[1]) to + 3°; $n_{D25°}$ about 1.445; soluble in less than 1 part of 90 p.c. alcohol.

[1]) In oils of our own drawing we have observed laevo-rotation down to — 2° 30′. *Report* April **1915**, 39.

Oil of Cinnamon *(Oleum Cinnamomi).* Yellow when freshly distilled, gradually becoming reddish; $d_{15.5°}$ 1.000 to 1.030[1]); α_D — 0,5 to — 1°; $n_{D25°}$ 1.565 to 1.580; soluble in 3 to 4 parts of 70 p.c. alcohol; one drop dissolved in 5 cc.[2]) of 90 p.c. alcohol assumes a pale green, but not a blue or brown coloration, on the addition of 1 drop of ferric chloride (absence of Cinnamon leaf oil and Cassia oil); contains from 55 to 65 p.c. of cinnamic aldehyde[3]) (determined with neutral sodium sulphite).

[1]) According to our observations with oils of our own drawing, specific gravity ranges between 1.023 and 1.040.

[2]) The desired reaction will only take place when 5 drops, and not 5 cc., of alcohol are taken.

[3]) In oils of our own drawing we have always observed an aldehyde content of 65 to 76 p.c. A specific gravity below 1.023 and an aldehyde content of less than 65 p.c. points to distillation having been carried out in an unsuitable way, and with unsuitable plant. We have touched upon this subject exhaustively in our *Report* October **1910** (p. 35) and cannot help expressing our surprise at the British Pharmacopoeia having utterly ignored our statements; in fact it makes it a point to exclude from the B. P. pure oils such as we obtain here from our own distillation. Such an astounding lack of impartiality on the part of the Pharmacopoeia commission speaks volumes for the spirit by which its deliberations were guided.

We gather from an English contemporary [*Perfum. Record* **6** (1915) 93] that serious difficulties have been encountered in England in obtaining cinnamon oils of the required low specific gravity and showing the correct solubility. On this occasion it is once again pointed out that the heavier cinnamon oils of continental make are probably adulterated with cinnamic aldehyde! As we are the principal manufacturers of this article, we must resent such an unheard-of calumny as far as our own oil is concerned, a calumny which is founded on nothing but ignorance or a biased mind, or both.

Oil of Cloves *(Oleum Caryophylli).* Colourless or pale yellow when fresh, becoming darker with age; $d_{15.5°}$ 1.047 to 1.065; $n_{D25°}$ 1.528 to 1.540[1]); soluble in 3 parts of 70 p.c. alcohol, the solution yielding a blue colour with ferric chloride; eugenol content not less than 85 p.c. (test with a 5 p.c. solution of potassium hydroxide).

[1]) In the introduction to this chapter we gave vent to our surprise at the rotation having been left unconsidered with clove oil. On the other hand, the refractive index could have been ignored. Clove oil has a slight laevo-rotation, α_D up to — 1° 35′.

Oil of Copaiba *(Oleum Copaibae).* Colourless or pale yellow; $d_{15.5°}$ 0.896 to 0.910; α_D — 7 to — 35°; $n_{D25°}$ 1.494 to 1.500; distils between 250 to 275°; test for gurjun oil (a solution of 1 cc. of oil in 5 cc. of glacial acetic acid does not develop more than a faint violet coloration on the addition of 4 drops of nitric acid), and for oil of

African copaiba (when distilled in a vacuum, the first 10 p.c. of the distillate has an optical rotation lower than that of the original oil)[1]).

[1]) This test serves in the first place for testing for gurjun balsam oil. Its reliability has, by the way, been questioned by Parry. *Chemist and Druggist* **80** (1912), 19.

Oil of Coriander *(Oleum Coriandri)*. Colourless or pale yellow; $d_{15.5°}$ 0.870 to 0.885; α_D + 8 to + 14°; $n_{D25°}$ 1.463 to 1.467; soluble in 3 parts of 70 p.c. alcohol.

Oil of Cubebs *(Oleum Cubebae)*. Colourless, pale green or greenish-yellow; $d_{15.5°}$ 0.910 to 0.930; α_D — 25 to — 40°; $n_{D25°}$ 1.486 to 1.500; not less than 60 p.c. distils between 250 and 280°.

Oil of Dill *(Oleum Anethi)*. Colourless or pale yellow, darkening on keeping; $d_{15.5°}$ 0.900 to 0.915; α_D + 70 to + 80°; $n_{D25°}$ 1.483 to 1.488; soluble in 3 parts of 90 p.c. alcohol.

Oil of Eucalyptus *(Oleum Eucalypti)*. Colourless or pale yellow; $d_{15.5°}$ 0.910 to 0.930; α_D — 10 to + 10°; soluble in 5 parts of 70 p.c. alcohol; contains not less than 55 p.c. of cineol (phosphoric acid method)[1]); test for phellandrene; oils containing much phellandrene are excluded.

[1]) Compare with what we said on the subject when discussing cajuput oil.

Oil of Siberian Fir *(Oleum Abietis)*. Colourless or nearly so; $d_{15.5°}$ 0.900 to 0.920[1]); α_D — 32 to — 42°[2]); $n_{D25°}$ about 1.474; contains from 30 to 40 p.c. of esters, calculated as bornyl acetate.

[1]) The higher limit of value is too low, the specific gravity goes up to 0.925.

[2]) The rotation of Siberian fir oil varies between — 37 and — 43°.

Oil of Juniper *(Oleum Juniperi)*. Colourless or pale yellowish-green; $d_{15.5°}$ 0.862 to 0.890[1]), increasing with age; α_D — 3 to — 15°; $n_{D25°}$ 1.472 to 1.488; when freshly distilled it is soluble in 4 parts of a mixture of equal volumes of 90 p.c. and absolute alcohol, the solubility decreasing with age.

[1]) 0.860 would have been more correct as the lower limit of value, so as to do justice to the Hungarian oil which has been taken into consideration in the limits for the rotation.

Oil of Juniper, empyreumatic see Oil of Cade.

Oil of Lavender *(Oleum Lavandulae)*. Pale yellow or yellowish-green; $d_{15.5°}$ 0.883 to 0.900; α_D — 3 to — 10°; soluble in 4 parts of 70 p.c. alcohol; contains from 7 to 11 p.c. of esters (English oil), or not less than 30 p.c. of esters (foreign oil), calculated as linalyl acetate[1]).

[1]) From these requirements it becomes evident that French as well as English distillates are now official.

Oil of Lemon *(Oleum Limonis)*. Pale yellow; $d_{15.5°}$ 0.857 to 0.860[1]); α_D + 58[2]) to + 64°; $n_{D25°}$ 1.473 to 1.476; citral content not less than 4 p.c. (determined with hydroxylamine)[3]).

[1]) 0.861 would be more correct as the higher limit of value.

[2]) Lower rotations occur repeatedly (down to 57°), in fact there were years when the bulk of arrivals rotated between + 54 and + 56°. Comp. *Report* October **1913**, 52.

[3]) In our *Report* October **1909**, 154, where we discussed the hydroxylamine method, we pointed out, that the values obtained thereby are about 10 p.c. too low, calculated on the citral present in the oil. We would like once again to lay stress on this fact, as in cases where the actual citral content of the oil borders on the lowest limit, results will be found with hydroxylamine which must lead to a rejection of the oil, whereas such a verdict would really be due to the incorrectness of the method. Moreover, it should not be forgotten that even with otherwise good oils a somewhat lower citral content may occur every now and then; the test should not, therefore, be applied too rigourously (comp. *Report* April **1914**, 59). It may here be called to mind that the above-mentioned B. P. requirement has given rise to a controversy as to citral content of

lemon oil between A. H. Bennett, H. E. Burgess and R. Doumin [*Perfum. Record* **5** (1914), 440; **6** (1915), 30, 37]. The question was also touched upon as to how much citral remains in the terpenes when manufacturing terpeneless oil. According to Bennett's observations this amounted to about 1.5 p.c., whereas Burgess considers 0.5 p.c. to be the maximum, Doumin being unable to prove the existence of any oxygenous parts at all in the lemon oil terpenes examined by him. Apart from this, there was nothing new in the discussion.

Oil of Lemongrass *(Oleum Graminis citrati)*. Dark yellow[1]); $d_{15.5°}$ 0.880 to 0.905; α_D — 3[2]) to + 3°; contains not less than 70 p.c. of aldehydes (sulphite method).

[1]) The colour is yellowish to reddish-brown.

[2]) In Malabar oils we observed rotations down to — 5°.

Menthol *(Menthol)*. M. p. 42 to 43°[1]); entirely volatilised by the heat of a water-bath; very slightly soluble in water, but readily soluble in 90 p.c. alcohol, the solutions being neutral to litmus. Boiled with sulphuric acid diluted with half its volume of water, menthol acquires an indigo-blue or ultramarine colour, the acid becoming brown.

[1]) The melting point lies between 42 and 44°.

Methyl salicylate *(Methyl salicylas)*. Colourless; sparingly soluble in water, readily soluble in 90 p.c. alcohol, in glacial acetic acid and in carbon disulphide; b. p. 219 to 221°; $d_{15.5°}$ 1.185 to 1.192; $\alpha_D \pm 0°$; ester content not less than 98 p.c.[1]); the alcoholic solution is neutral or faintly acid, the aqueous solution is coloured violet by the addition of one drop of ferric chloride.

[1]) For the *complete* saponification two hour's heating on the water-bath is required with methyl salicylate, lest the values obtained be too low.

Volatile Oil of Mustard *(Oleum Sinapis volatile)*. Colourless or pale yellow; $d_{15.5°}$ 1.014 to 1.025; distils between 148 to 156°; allyl*iso*thiocyanate content not less than 92 p.c.

Oil of Nutmeg *(Oleum Myristicae)*. Colourless or pale yellow; $d_{15.5°}$ 0.870 to 0.925; α_D + 13[1]) to + 30°; $n_{D25°}$ 1.474 to 1.484; soluble in 3 parts of 90 p.c. alcohol; evaporation residue not more than 5 p.c.

[1]) The lower limit of value is too high, for we have observed rotations of + 7° 52′ in oils distilled by ourselves from the best raw material. Compare *Report* October **1904**, 65.

Oil of Peppermint *(Oleum Menthae piperitae)*. Colourless, pale yellow or greenish-yellow; $d_{15.5°}$ 0.900 to 0.920; α_D — 20 to — 35°; soluble in 4 parts of 70 p.c. alcohol; total menthol not less than 50 p.c., menthyl acetate not less than 5 p.c.[1]).

[1]) According to our own observations, ester percentage may be as low as 4 p.c. with best oils.

Oil of Rose *(Oleum Rosae)*. A pale yellow or yellowish-green, crystalline mass; semi-solid at ordinary temperatures; $d^{30°}_{15.5°}$ 0.854 to 0.862[1]); α_D — 2 to — 4°[2]); $n_{D25°}$ 1.456 to 1.465; m. p. 20 to 23°.

[1]) The lower limit of value is not correct, good Bulgarian oils have a specific gravity down to 0.849. We have pointed this out on previous occasions (*Report* April **1910**, 127).

[2]) We have often observed rotations down to — 1° with oils of irreproachable quality. Oils showing a higher rotation than — 2° 30′ should be regarded with suspicion (comp. *Report* April **1912**, 108).

Oil of Rosemary *(Oleum Rosmarini)*. Colourless or pale yellow; $d_{15.5°}$ 0.895 to 0.920; α_D — 2 to + 15°; $n_{D25°}$ 1.463 to 1.473; soluble in 1 part of 90 p.c. alcohol and in 5 to 10 parts of a mixture of equal volumes of 90 and 70 p.c. alcohol; total borneol at least 10 p.c.; ester (bornyl acetate) at least 1.8 p.c.[1]).

[1]) In accordance with facts, the lowest limit for total borneol ought to be reduced to 8 p.c., and ester down to 1 p.c.

Oil of Sandalwood *(Oleum Santali)*. Nearly colourless or pale yellow; $d_{15.5°}$ 0.973 to 0.985; α_D — 13 to — 21°; $n_{D25°}$ 1.498 to 1.508; soluble in 6 parts of 70 p.c. alcohol at 20°; total santalol ($C_{15}H_{24}O$) not below 90 p.c.

Oil of Spearmint *(Oleum Menthae viridis).* Colourless, pale yellow, or greenish yellow, becoming darker on keeping; $d_{15.5°}$ 0.925 to 0.940[1]); α_D — 30 to — 50°; soluble in 3 parts of 90 p.c. alcohol; forms a clear solution with one part[2]) of a mixture of equal volumes of 90 and of 70 p.c. alcohol, the solution becoming turbid on further dilution.

[1]) The lower limit of value is too high, it should be 0.920.

[2]) To effect a solution, 1 to 1½ parts are required at 20°.

Terebene *(Terebenum).* Mixture of dipentene with other hydrocarbons, obtained by shaking turpentine oil with successive quantities of sulphuric acid until optically inactive and then distilling in a current of steam.

Colourless; $d_{15.5°}$ 0.862 to 0.866; α_D + 1 to — 1°; soluble in 5 parts of 90 p.c. alcohol; it distils between 156 to 180°, leaving only a slight viscous residue; not more than 15 p.c. distils below 165°.

Thymol *(Thymol).* M. p. 50 to 51°; completely volatilized on a water-bath; almost insoluble in water, readily soluble in 90 p.c. alcohol, in ether and in solution of sodium hydroxide. A solution of thymol in half its volume of glacial acetic acid, warmed with an equal volume of sulphuric acid, assumes a reddish-violet colour.

Rectified Oil of Turpentine *(Oleum Terebinthinae rectificatum).* Colourless; $d_{15.5°}$ 0.860 to 0.870; $n_{D25°}$ 1.465 to 1.480; distils almost entirely between 156 and 180°[1]) leaving no appreciable residue.

[1]) The bulk of rectified turpentine oil must distil up to 165°.

Oil of Wintergreen *(Oleum Gaultheriae).* Distilled from the leaves of *Gaultheria procumbens* or from the bark of *Betula lenta.* Colourless or nearly so; $d_{15.5°}$ 1.180 to 1.187[1]); α_D 0 to — 1°; n_D 1.537 to 1.539; soluble in 6 parts of 70 p.c. alcohol[2]) at 25°; contains not less than 99 p.c. of methyl salicylate[3]).

[1]) The specific gravity of gaultheria oil ranges up to 1.193.

[2]) At 20° 6 to 8 volumes of 70 p.c. alcohol are required.

[3]) With genuine gaultheria oil, ester percentages as low as 96 p.c. have been met with. As regards duration of the saponification, the same applies as stated when discussing artificial ester.

Oil of Wintergreen, artificial see Methyl salicylate.

Finnish Pharmacopoeia.

(Pharmacopoea Fennica V.)

In its indications for essential oils, the Finnish Pharmacopoeia confines itself mostly to colour, odour, specific gravity and solubility. As these are without exception in accordance with recognized facts, all we have to do is to reproduce the requirements laid down for the various oils. We may add that the solubility test requires a *Spiritus* of 90 to 91 p.c., and a *Spiritus dilutus* of 69.8 to 70.6 p.c. by volume.

Oil of Anise *(Aetheroleum anisi).* Colourless or pale yellow; congeals at about 17° to a white crystalline mass[1]); $d_{20°}$ 0.98 to 0.99; soluble in 3 parts of *Spiritus.*

[1]) The oil does not always congeal of its own accord. In case of need a little solid oil, or anethol, should be added to the chilled oil. With age, anise oil loses its crystallizing capacity under the influence of light and air, until finally it does not congeal any more.

Camphor *(Camphora).* M. p. 175 to 179°; sparingly soluble in water, readily so in *Spiritus,* ether, chloroform, fixed and essential oils; when heated even moderately it sublimes without leaving any residue.

Oil of Cinnamon, Ceylon *(Aetheroleum cinnamomi).* Pale yellow; $d_{15°}$ 1.023 to 1.040; soluble in 3 parts of *Spiritus dilutus.*

Oil of Cloves *(Aetheroleum caryophylli).* Nearly colourless or yellow, becoming darker with age; $d_{15°}$ 1.044 to 1.070; soluble in 2 parts of *Spiritus dilutus.*

Oil of Fennel *(Aetheroleum foeniculi).* Colourless or pale yellow; $d_{15°}$ 0.965 to 0.975; soluble in 1 part of *Spiritus;* when cooled below 0° the oil separates crystals[1]).

[1]) Fennel oil does not always become solid of its own accord when cooled, but it becomes solid at once if a particle of solid fennel or anise oil, or anethol, is added to the chilled oil. When improperly stored, the congealing point of the oil becomes lower, until finally it does not congeal any more. Comp. *Report* October **1904**, 42.

Oil of Lemon *(Aetheroleum citri).* Light yellow; $d_{15°}$ 0.855 to 0.861; almost completely soluble in 12 parts of *Spiritus.*

Menthol *(Mentholum).* Colourless, brittle crystals, almost insoluble in water, readily soluble in *Spiritus,* ether, chloroform, and fixed oils. M. p. 43 to 44°[1]); when pressed between filtering paper no spots should appear on the paper. 0.5 g. of menthol should sublime on the water-bath without leaving any weighable residue.

[1]) The melting point lies between 42 and 44°.

Oil of Mustard *(Aetheroleum sinapis).* Colourless or pale yellow, becoming darker with age; $d_{15°}$ 1.022 to 1.025[1]); soluble in every proportion of *Spiritus.*

[1]) As the pharmacopoeia does not make any statements as regards process of manufacture, the natural as well as the artificial oil may be used, if the latter has the required specific gravity. The limits have been drawn a little too narrow, with the natural oil they lie between 1.016 and 1.022, and with the artificial oil between 1.020 and 1.025.

Oil of Peppermint *(Aetheroleum menthae).* Colourless or yellowish. $d_{15°}$ 0.90 to 0.91.

Oil of Rose *(Aetheroleum rosae).* Colourless or pale yellow; $d_{30°}$ 0.85 to 0.863; at 18° it begins to separate crystals and congeals little by little to a crystalline mass.

Oil of Sandalwood, East Indian *(Aetheroleum santali).* Colourless or pale yellow; $d_{15°}$ 0.973 to 0.985; soluble in 6 parts of *Spiritus dilutus,* the solution should remain clear even when further diluted.

Thymol *(Thymolum).* Colourless crystals, soluble in about 1100 parts of water and in 100 parts of glycerin, readily soluble in *Spiritus,* ether, chloroform, fixed and volatile oils as well as in soda lye; m. p. 50 to 52°; 0.5 g. of thymol should sublime on the water-bath without leaving a residue. Identity reactions and test for phenol.

Oil of Turpentine, rectified *(Aetheroleum terebinthinae).* Colourless; $d_{15°}$ 0.860 to 0.870; boiling temperature 155 to 162°; soluble in 8 parts of *Spiritus,* the solution should not give an acid reaction.

Chemical Preparations and Drugs.

Almond Oil, expressed, from apricot kernels. A few statistical data have been published about the apricot kernel industry in China[1]). In 1912, China exported 44479 piculs, or about 5930500 lbs., 80 p.c. of which were exported from Tientsin. The bulk finds its way to Europe, where Germany, Great Britain, France and Italy are the largest buyers. Of the 4801200 lbs. exported from Tientsin in 1912, 3199400 lbs. were sweet kernels, and 1601800 lbs. were of the bitter variety. The apricots ripen in June, the shipping season begins in August and continues through the remainder of the year. The apricots from which sweet kernels are obtained are larger than those from which come the bitter kernels. These apricots are not edible.

The cracking of the seeds and extracting of the kernels is all done by hand with a wooden hammer, the seeds being first soaked in water to moisten them. Dried apricots do not appear to be exported from China.

Civet. Some years ago we isolated from natural musk a ketone $C_{15}H_{28}O$ or $C_{16}H_{30}O$, which we called muskone and which is the sole bearer of musk odour[2]). A similar body, equally a ketone, of the composition $C_{17}H_{30}O$, has now been found in civet by E. Sack[3]). He calls this ketone Zibetone (civetone). It possesses a fine musk-like odour which is very lasting and clinging. To isolate civetone, Sack boils civet for several hours with strong alcoholic potash lye, distils off the alcohol, treats the residue with water and extracts the solution with ether. The ether is distilled off and thereupon the residue is distilled with steam until no more skatol passes over. Again ether extraction is resorted to, the ether again distilled off, at last *in vacuo,* and the remaining oil is then treated with a little alcohol. After renewed filtering the filtrate is distilled, at last *in vacuo,* to eliminate the alcohol. Finally there remains a light yellow to brownish black syrup representing about 10 to 15 p.c. of the civet used. It shows a pronounced musk odour, but at the same time the characteristic civet or animal odour = *odeur de bête.* Equal parts are now mixed of this extract, of semicarbazide hydrochloride and sodium acetate, along with a little alcohol, the resulting mixture being allowed to stand for about 24 hours. The tough mass which results is mixed with a lot of water, the strongly oily crystals are separated from the oil by filtration and immersed in ligroin (boiling below 100°). In this process the oily particles are dissolved, whereas the semicarbazone settles. After a second washing with ligroin and drying on a porous tile, and finally on the water-bath, it shows the m. p. 182°. After re-crystallization from 96 p.c. alcohol it melts at 187°. By combustion the crude formula $C_{18}H_{33}ON_3$ was established for the semicarbazone. By treating the semicarbazone with alcoholic sulphuric acid or by heating with concentrated hydrochloric acid, civetone may easily be obtained in the pure state. It forms a colourless oil, which readily congeals in the pure state to an ice-like crystalline mass, m. p. 32.5°. B. p. 204 to 205° (16.5 to 17 mm.); 342° (741.5 mm.). The analytical figures agreed with the formula $C_{17}H_{30}O$. Civetone readily volatilizes with steam and is indifferent toward alkali and acids. It may therefore be obtained from civet by distilling the latter with alkali, the distillate being treated with semicarbazide. The oxime melts at 92°.

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[1]) *Perfum. Record* **5** (1914), 365. — [2]) *Report* April **1906**, 94. — Walbaum, *Journ. f. prakt. Chem.* II. **73** (1906), 488. — *D. R. P.* 198660 of July 15th, 1905. — [3]) *Chem. Ztg.* **39** (1915), 538. — Compare *D. R. P.* 279313.

According to Sack it is not improbable that, as many animals and plants show natural musk aroma, a long list of natural musk bodies will be found yet, just as we know a long list of artificial musk bodies.

Coumarin. L. A. Jordan and J. F. Thorpe[1]) report on the formation of coumarin derivatives and the production of stable coumarinic acids. As only very complicated coumarin derivates are included, we confine ourselves to draw the attention to the voluminous treatise.

When phenols are oxidized in alkaline solution with persulphates, a new hydroxyl enters in *p*-position, or, if *p*-position is already occupied, in *o*-position to the first-named hydroxyl. G. Bargellini and L. Monti[2]) have now studied the influence of persulphates on coumarins. At ordinary temperatures, and in alkaline solution, coumarin yields with potassium persulphate in the presence of a little ferrous sulphate 5-hydroxycoumarin of the m. p. 248 to 250°. The oxidation of a few coumarin derivatives is described, but for further particulars we must refer to the original paper.

Musk, Tonkin. The statistical figures for the year 1914 for the exports of musk from Shanghai are now before us; they are as follows: —

Year	Paris	London	New York	Germany and Austria	Total
	Catties	Catties	Catties	Catties	Catties
1914	260	94	250	14	618
as against					
1913	260	127	308	14	709
1912	320	183	287	36	826
1911	416	155	316	20	907
1910	722	239	287	65	1313
1909	480	181	186	60	887

Below we give the figures covering the musk exports of the first half of 1915: —

Jan./June	Paris	London	New York	Germany and Austria	Total
	Catties	Catties	Catties	Catties	Catties
1915	10	23	377	—	410
as against					
1914	255	94	136	14	499
1913	208	121	297	14	640
1912	132	107	126	20	385

The only feature worthy of note is the decrease of the business with Paris and London as compared with the considerable increase in the turnover with New York. Our friends are of opinion that this might be due to the fact that since the beginning of the war the French and English perfumery industry have been pushed out of many

[1]) *Journ. Chem. Soc.* **107** (1915), 387. — [2]) *Gazz. chim. ital.* **45** (1915), I. 90; *Chem. Zentralbl.* **1915**, I. 1116.

of their markets by the Americans, especially so in central and southern America. It is impossible to say whether this surmise is correct or whether, perhaps, New York has merely become the place of transit for the quantities of musk now shipped to Europe in an easterly direction.

Thymol. This preparation belongs to the list of articles the manufacture of which, at competitive prices, had been found possible in Germany only, and it was therefore not to be wondered at that the principal consuming countries, namely England and the United States, were placed in an awkward position through the outbreak of the war. Prices soon reached a fabulous level, and as appears from the technical press, all attempts abroad to take up the manufacture on a large scale proved to be failures so far.

The *Chemist and Druggist*[1]) writes as follows: "The production of this phenol from ajowan-seed oil has not proved to be a complete success in this country so far, and there appears to be no immediate hope of the scarcity being relieved or the market price reduced. The present is an excellent opportunity for manufacturers in India, who profess to have surmounted all the difficulties of thymol-production, to capture the world's markets, at least the British and American." In the latter connection we note that the U. S. A. Commerce Reports for August 9 contain a despatch by Commercial Agent Thomas H. Norton on the very pronounced scarcity of thymol in the American market, and the despatch deals also with the source and manufacture of thymol. In regard to this he says:—

> "The extraction of the essential oil present in the seeds is usually effected in large stills, of a capacity of at least 600 gals. The seeds are introduced in cages or trays, which occupy the interior, and a current of live steam is passed through the still. The oil, carried along with the steam, condenses with it and floats upon the surface of the water of condensation, from which it is drawn off. This water is used repeatedly in the production of steam, in order to avoid any loss of the small amount of oil held in solution. The yield of oil from 100 lbs. of ajowan-seed varies from 3 to 4 lbs. Ajowan oil consists of thymol to the extent of from 40 to 55 p.c., accompanied by cymene, and by a terpene hydrocarbon. A separation from the two hydrocarbons is effected by agitation with a solution of caustic soda, in which the thymol dissolves in the form of its sodium salt. From the alkaline solution the thymol is precipitated by the addition of hydrochloric acid. The crude thymol is purified by crystallization from alcohol or glacial acetic acid. It has also been found practicable to submit the oil to fractional distillation and extract the thymol from the higher-boiling fractions by the application of cold. Pure thymol boils at 230° C. A large amount even can be obtained directly from the oil by exposing to freezing-mixtures".

Dr. Norton adds that "the amount of thymol obtainable by this process from the annual export of ajowan-seeds from India is estimated at 20 long tons". The thymol may be "obtainable", but is not obtained, and the conventional process, given with modifications, is probably one of the reasons for this. Indeed, what American and British would-be makers of thymol want is a few "tips" as to how to turn out nice white crystals like the German product. It may be that the latter was partly synthetic, but ajowan thymol was unquestionably the principal part of the German output".

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[1]) 87 (1915), 340.

To this we need only add that we quite agree that "a few tips" will still be necessary to convert the theory described into practice. Everybody here in Germany, who has anything to do with thymol manufacture, will hardly be able to take cognizance, without a smile, of these rather naive remarks.

In view of the present scarcity of ajowan oil, steps appear to have been taken in England to find other sources for thymol, for we find[1]) that the firm of H. Rubeck in London has placed on the market a thymol obtained from thyme oil. There is nothing remarkable in this fact, for there is no reason why thymol should not be produced from this raw material in England or elsewhere. But if, in reference to this particular article, we read that the production of thymol crystals is attained "by an extremely ingenious process", it is somewhat amusing to learn that Rubeck's preparation suffices perhaps for practical purposes, but that its melting point is too low and does not, therefore, come up to the requirements of the British Pharmacopoeia. The reason given is that "under present excise conditions" thymol cannot be crystallized from pure alcohol in England. There is little consolation in this for the buyer. It is evident that the writer of the article was in an awkward predicament, for on the one hand he was obliged to bestow praise upon the "ingenious" manufacturer, on the other hand he felt compelled to draw buyers' attention as "gingerly" as possible to the evident defects of this "ingenious" product.

Vanillin. In our previous *Report* (p. 60) we mentioned a publication by M. Lehmann on his observations in the examination of vanillin from clove oil on the one hand, and from guaiacol on the other hand. As the vanillin produced in the latter way came off second best in the paper in question, the firm of C. F. Boehringer & Söhne were induced to publish a reply, in which they proved that vanillin may be produced from guaiacol in equal purity and quality as from eugenol. In a letter to the editor of the *Chemiker-Zeitung* [**39** (1915), 266], Lehmann now replies that in his paper he spoke of guaiacol vanillins in quite a general way, and that he never implied that there are no such preparations which are not equal to clove oil vanillin. In their reply Messrs. Boehringer & Söhne declare themselves satisfied with this statement.

J. F. Sacher[2]) has also been occupied with the solution of above question and has arrived at the same conclusion, viz., that vanillin may be produced from guaiacol in exactly the same purity and of the same quality as from eugenol. Sacher carried out his examination in the following manner: about 0.5 g. of vanillin are weighed exactly, and are dissolved in about 100 cc. of absolute alcohol previously neutralized, and, by using phenol phthaleine as indicator, are titrated with alcoholic N/10 soda lye. In this manner he found values from 99.85 to 100.2 p. c. with vanillins originating partly from Franz Fritzsche & Co., from which he concludes that the preparations in question were of the required degree of purity. It is said that adulterations may be readily found by titration, and it is alleged that fractions of percents of foreign bodies (acetanilide, heliotropin, sugar, benzoic acid, phthalic acid) can be proved with accuracy in this manner.

Unfortunately we have failed to obtain similarly satisfactory results with this method. We cannot agree with the opinion of Sacher that, by using phenolphthaleine as indicator, vanillin may be titrated correctly with alkali liquor. The same drawback is noticeable which is opposed to a correct determination of phenols by direct titration with alkali, viz., the weak acid character of phenol as opposed to the strong base.

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[1]) *Perfum. Record* **6** (1915), 55. — [2]) *Deutsche Parf.-Ztg.* **1** (1915), 187.

It is due to this fact that the solution begins to show alkaline reaction even before the phenol is completely bound to the alkali. Therefore there is no sudden change from colourless to red, but a gradual transition through pink takes place and it is difficult to say which particular shade of colour is to be considered as the end of the reaction. A correct result cannot be obtained in this manner. If titration is stopped as soon as the first permanent pink coloration is observed, values are found, even with pure vanillin, which are invariably below 100 p.c.; the figures ascertained by us ranged between 96 and 98 p.c. We consider it quite out of the question that even fractions of percents of foreign matter could be proved in vanillin in the above-described manner; on the contrary, it may happen that quite a wrong verdict is arrived at if the examination is confined to titration.

Notes on Scientific Research in the Domain of the Terpenes and Essential Oils.

General.

Selection of aromatics for covering nasty smells.

How nasty smells may be covered with the aid of synthetic aromatics has been discussed by R. Marchand in a short article[1]). As even the finest flower odours always contain subtances which in themselves have a disagreeable smell, the direction is given which one has to follow in order to cover a smell successfully. Jasmin, e. g. contains indole, which in itself smells of faeces. If therefore a faecal-like odour has to be covered, it can best be done with artificial jasmin free from indole. Very often the odour of fish oil has to be covered. If one takes into consideration that white hawthorn contains a body of a similar smell as fish oil, one comes to the conclusion that odoriferous substances of the white hawthorn class, such as aubépine and *p*-cresol methyl ether may serve to cover the odour of fish oil. Once the odour is covered, other substances may be added in order to obtain a different perfume.

The odour of light petroleum ought not always to be covered with the aid of turpentine oil, but the selection should thus be made that the perfume is adequate to the final product in view. When turpentine is cheap, one often tries to cover its odour. If articles like boot polish, leather grease, &c., are concerned, Russia leather perfume is most appropriate.

The chemistry of colloids and the manufacture of perfumes.

P. Rohland[2]) has published an article on the importance of the chemistry of colloids for the perfume industry. The most interesting feature in it is the absorption of odours by colloids and of bodies inclined to become colloidal. The absorptions are due to the fact that these bodies, especially in contact with water, form and contain numerous colloidal substances, which have to be considered as dense tissues.

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[1]) *Deutsche Parf.-Ztg.* **1** (1915), 160. — [2]) *Deutsche Parf.-Ztg.* **1** (1915), 116.

Kaolin and clay, used for giving body to soap, belong to the substances inclined to be colloidal. If ammonia solution is shaken with kaolin, it takes the characteristic smell of kaolin, whereas the kaolin smells of ammonia.

Talc (magnesium silicate) is most sensitive in this respect. It absorbs perfumes in a very short time, and if it is then rubbed on the hands the smell lasts considerably longer than if the perfume itself had been used.

Bibliography.

In April this year the first number was published of the *Deutsche Parfümerie-Zeitung, Zentralorgan zur Förderung deutscher Parfümerie-Erzeugnisse und verwandter Artikel.* The edition of a periodical of importance in this line is to be welcomed with joy, the more so as such a one did not exist here so far. The fact that its publication started during the great war is a sign of the favourable economic condition of our country.

H. Schelenz published in the *Deutsche Parfümerie-Zeitung* [Vol. **1** (1915), 29, 52, 75, 97, 117, 139, 161, 224] an article entitled "Contributions to the Knowledge about Cosmetics in the sixteenth century (according to Shakespeare's works)", in which there are to be found numerous interesting indications as to the use of perfumes and cosmetics in antiquity and the middle ages.

There is an annual report by A. Reclaire in the *Zeitschrift für angewandte Chemie* [Vol. **28** (1915), I. 369] on the progress in the chemistry of essential oils and aromatics.

E. Kremers[1]) rendered in a clear and concise manner the most important facts out of the section "Cymbopogon oils" of the book *The Volatile Oils.* After an introduction he discusses the history and the production of these oils and then gives in the form of tables a review of the occurrence of the components, of the composition of the oils and, with the aid of the structural formulas, of the relationship of the most frequent components. He thinks that such a digest of the whole book will facilitate for the student of chemistry and the pharmacist the understanding of the interesting domain of the essential oils.

Analytical Notes.

Beilstein's copper oxide test for halogens.

In order to test synthetic camphor for chlorinated products, E. Richter[2]) recommends, as Stephan[3]) did some years ago, Beilstein's copper oxide method, but does not use solid copper oxide, as Beilstein indicates, but a piece of copper wire netting of 1:0.5 cm. H. Kunz-Krause[4]) thinks it more correct, however, to adhere to Beilstein's original prescription, as the oxygen of the copper oxide is necessary for the formation of the copper halide, for which a body consisting entirely of copper oxide offers better guarantees than copper wire netting, which will always be oxidized on the surface only. If the test is carried out with copper oxide pieces, natural camphor and synthetic camphor free from chlorine do not show the slightest trace of green colouring. However, copper wire netting being used instead of copper oxide, now and then, at

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[1]) *The Druggist's Circular*, June **1915**, p. 355. — [2]) *Apotheker Ztg.* **30** (1915), 14. — [3]) *Berichte d. deutsch. pharm. Ges.* **19** (1909), 228, 230; *Report* October **1909**, 33. — [4]) *Apotheker Ztg.* **30** (1915), 141.

the beginning of the heating, a bluish-green colouring of the flame, though feeble and transitory only, due to the copper, was noticed, especially when the camphor was heated over a small flame.

Kunz-Krause points out that from the appearance of a green or bluish-green colouring in Beilstein's test one must not always conclude that halogens are present, as it may occur that the substance tested forms more or less volatile compounds with copper. This is the case e. g. with benzoic acid, the copper benzoate formed on heating with copper oxide being sufficiently volatile to colour the flame bluish-green, so that it looks as if halogens were present in the acid. Only a check test with a substance unquestionably free from halogens can give a clue as to the significance of such a colouring.

Very interesting is the observation which Kunz-Krause made with camphoric acid and which shows the reciprocal pyrochemical decomposition in Beilstein's test. Camphoric acid does not yield any volatile copper compound and therefore leaves the Bunsen flame unchanged. But if the acid, spread out on the cover of a porcelain crucible, is touched with glowing-hot copper oxide, even with the smallest fragment of a crystal, an intensely nickel-green spot is immediatelly formed. The reaction is due to the pyrogenous formation of copper camphorate. If terpine hydrate is used instead of camphoric acid, it is said that under the same conditions a decomposition product of a pronounced benzaldehyde odour results, an indication which we have not been able to confirm on checking the test.

Critical examination of the most important methods for the evaluation of mustard oil.

The prize problem of The Hagen-Bucholz Fund of the *Deutscher Apotheker-Verein* for the year 1912/13 was: Comparative investigations as to the evaluation of *Semen Sinapis, Spiritus Sinapis, Oleum Sinapis* and *Charta sinapisata* according to the various methods indicated for the purpose. With reference to this, H. Frerichs reports on the investigations of F. Wehrmann, K. Wegener, F. H. Braunwarth, and K. Meyer. The treatises of Wehrmann and Wegener contain a great number of practical experiments, but in which only the best-known methods have been taken into consideration. Meyer carried out but few practical experiments, and Braunwarth considered the problem more a literary than a practical one. Frerichs reports especially on Wehrmann's treatise, leaving out everything superfluous.

According to the 2nd and 3rd editions of the German Pharmacopoeia, allyl mustard oil must be determined as thiosinamine[1]). From the results obtained by Wehrmann, it is evident that the method is fairly correct, but it can hardly be used in practice, because of the comparatively great waste of material and, on the other hand, because it is applicable almost exclusively to the evaluation of pure mustard oil and not for preparations of mustard seed.

According to Förster's method[2]), mustard oil is transformed into thiosinamine with the aid of ammonia, the sulphur precipitated with yellow mercuric oxide as mercuric sulphide and the oxydihydrargyriammoniumhydroxide, formed by the action of the excess of ammonia, extracted with potassium cyanide solution or nitric acid from the thiosinamine solution, to which the mercuric oxide had been added, before it cools down completely. The remaining mercuric sulphide is collected on a dried and weighed filter and then weighed at 100°, after having been washed and dried. Wehrmann

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[1]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 605. — [2]) *Landw. Versuchs-Stat.* **35** (1888), 209; *Untersuch. d. Nahrungs- u. Genussm.* **1** (1898), 235.

employed in his experiments freshly precipitated mercuric oxide, still suspended in water, as he had difficulties with the dry substance. The results obtained by Wehrmann after this method were little satisfactory, as he found partly too much, partly too little mercuric sulphide. Haselhoff[1]) arrived at the same result at the time.

Wehrmann did not verify E. Dieterich's[2]) method, as, according to the indications in the literature, reliable results cannot be obtained by it, but he checked the modification by K. Dieterich[3]). It is clear from his results that it has no essential influence on the final outcome, whether the mixture is heated or left cold. One seems to obtain somewhat better results by heating, which way is preferable too for the sake of speed.

It is striking that, following this method, too high results are sometimes obtained, a fact which Kuntze[4]) explains by the content of allylthiourethane in spirit of mustard, found especially in old preparations.

According to Gadamer[5]), it is unsuitable to add ammonia first and then silver nitrate, as it is the case in Dieterich's method, for some mustard oil can evaporate before the thiosinamine has formed. If on the contrary a mixture of strong ammonia with the necessary amount of silver nitrate is added at once, or if such a mixture is used in the receiver, the transformation into silver sulphide takes place more quickly and with greater certainty. When the reaction is completed, the mixture ought to be left standing for 12 hours, so that the silver sulphide can deposit. The results obtained by this method were very good, the exactness corresponding about to that of Dieterich's process, which, however, especially if heat is employed, has the advantage of greater speed.

The titrimetric test of the German Pharmacopoeia, 5th edition[6]), excels by its great exactness and reliability, says Wehrmann, and is easily carried out, as the N/10 silver nitrate solution is stable enough for the purpose of titration.

Roeser[7]) indicates a method which in its first part corresponds with that of the German Pharmacopoeia. The titration of the excess of silver nitrate is carried out according to Denigès. After Wehrmann's opinion, this method gives very good results and is also easily carried out. He prefers, however, the method given in the Ph. G., on account of the limited stability of the N/10 potassium cyanide solution.

After Dirck's process[8]) or its usual modification by Schlicht[9]), alkaline potassium permanganate solution is added to the mustard oil. The excess of permanganate is decomposed with alcohol, and the resulting sulphuric acid is determined in the filtrate as usual by precipitation with barium chloride, after acidulation with hydrochloric acid and the addition of a solution of iodine and potassium iodide until a slight yellow coloration results. Instead of potassium permanganate, Haselhoff[10]) also employed bromine water, thus obtaining better results.

On checking this test, Wehrmann found very different results. Evidently the oxidation of the sulphur is not always quantitative. Wehrmann did not arrive at satisfactory results when using bromine water as an oxidizing agent, as bromine does not oxidize mustard oil quantitatively, but partly transforms it otherwise. Oily drops of dibromo mustard oil, $C_3H_5Br_2NCS$, separate. This dibromo mustard oil escapes the analysis, as it is volatile with steam, and the precipitation of barium sulphate must be carried out in the heat, so that Wehrmann found too little mustard oil.

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[1]) *Zeitschr. Untersuch. d. Nahrungs- u. Genussm.* **1** (1898), 235. — [2]) Gildemeister and Hoffmann, *loc. cit.*, p. 607. — [3]) Gildemeister and Hoffmann, *loc. cit.*, p. 608. — [4]) *Arch. der Pharm.* **246** (1908), 58; *Report* April **1908**, 69. — [5]) *Arch. der Pharm.* **235** (1897), 58. — [6]) Comp. *Report* April **1911**, 129. — [7]) *Journ. de Pharm. et Chim.* VI. **15** (1902), 361; *Report* October **1902**, 52. — [8]) *Landw. Versuchs-Stat.* **28** (1883), 179. — [9]) *Zeitschr. f. anal. Chem.* **30** (1891), 661. — [10]) *Zeitschr. Untersuch. d. Nahrungs- u. Genussm.* **1** (1898), 235.

In conformity with Grützner's method[1]), mustard oil is not oxidized direct, but first transformed, with the aid of ammonia, into thiosinamine, which is then oxidized with sodium peroxide. Wehrmann allowed the sodium peroxide to act at first in the cold and then heated the mixture. For 1 g. of mustard oil he used 5 g. of sodium peroxide. The method affords very good results and is easily carried out.

In order to estimate mustard oil, one may likewise determine its content of nitrogen, for instance after Kjeldahl. For this purpose, Wehrmann weighed pure mustard oil in small bulbs, which he had made himself from a glass tube and sealed after having filled them. He broke such a bulb, in a vessel as recommended by Kjeldahl, below the required sulphuric acid, destroyed the mustard oil in the usual way and then determined the ammonia formed. From the quantity of nitrogen determined from the ammonia he then calculated the corresponding amount of mustard oil. The values found were fairly good, but the process is too complicated and suitable only for pure mustard oil, not for the evaluation of mustard oil in mustard seed.

Passon[2]) found that mustard oil may be distilled from oil-cake, mustard powder or mustard paper into glacial acetic acid, in which solution he determined the content of nitrogen according to Kjeldahl. One adds some powdered zinc or iron to the glacial acetic acid in the receiver, so as to bring about a partial reduction of the mustard oil to the amine. In order to avoid losses of mustard oil during the distillation, a vessel with a little concentrated sulphuric acid is connected with the receiver containing the glacial acetic acid. The solution of mustard oil in glacial acetic acid and the concentrated sulphuric acid are then united in a flask of the kind recommended by Kjeldahl for the purpose, and the content of nitrogen is determined in the usual way.

Wehrmann tested this method on a solution of mustard oil in alcohol and recovered in two experiments 98 and 99.6 p.c. of the mustard oil employed. As may be seen, the process gives good results, but it is very intricate, takes time and requires much practice.

The method recommended by Jörgensen[3]), after which not the mustard oil but the thiosinamine, obtained with the aid of ammonia, is determined according to Kjeldahl, has been examined by Wegener, who in two instances found 96.98 and 97.8 p.c. of the mustard oil used.

Wehrmann concludes from the results of his investigations that out of the methods, based upon oxidation of the sulphur, Grützner's is the most useful. As regards the methods for determining the sulphur as metallic sulphide, Dieterich's gives the best results, and the best titrimetric process is that prescribed by the German Pharmacopoeia, 5th edition.

Wegener verified some other tests, which Wehrmann had not taken into consideration.

Following Pleijel's method[4]), Wegener found 98.21, 97.82 and 98.6 p.c. of the mustard oil employed.

In the commentary to the German Pharmacopoeia, Fischer and Hartwich indicate Gadamer's prescription with the addition that the mixture of distillate, ammonia and N/10 silver nitrate solution ought to be heated to 80° after a 24 hours' standing. The results of three experiments were 98.27, 98.56 and 97.98 p.c.

Holz[5]) recommended the method of the German Pharmacopoeia, 4th edition, with the modification that the mixture of distillate, ammonia and silver nitrate solution

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[1]) *Arch. der Pharm.* **237** (1899), 185; *Report* October **1899**, 37. — [2]) *Zeitschr. f. angew. Chem.* **9** (1896), 422. — [3]) *Chem. Zentralbl.* **1898**, II. 927. — [4]) *Farmac. Revy* **1907**, 204; *Report* October **1907**, 64. — [5]) *Veröffentl. a. d. Gebiete d. Militär-Sanitätswes.* 1915, number 29.

ought to be thoroughly shaken, filled up to the mark, filtered immediately, and the excess of silver determined as the German Pharmacopoeia, 4th edition, indicates. According to this method, Wegener found only 82.73, 85.62 and 84.37 p.c. of the mustard oil used.

Pénau[1]) recommended to determine the excess of silver by weight as silver chloride, not titrimetrically by sulphocyanide solution. Wegener thus obtained 98.95 to 100.03 p.c. in four tests.

Following the indications of the Swedish Pharmacopoeia, 9th edition[2]), Wegener found in three cases 99.54 to 100 p.c. of the mustard oil used, whereas according to the prescriptions of the pharmacopoeias of the United States, 8th edition, Belgium and Russia, 6th edition far too low values were found.

As the result of his investigations regarding the question: In which way can the greatest yield of mustard oil be obtained from mustard seed and mustard seed preparations? Wehrmann states that the best yield is arrived at, and the investigation carried out most quickly and reliably, as follows: 5 g. of mustard powder are mixed with 100 g. of water and left standing for 2 hours, when 20 cc. of alcohol are added and, if necessary, 2 cc. of olive oil. The mixture is then distilled on a water-bath, preferably on a glycerin-bath of 120°, a Liebig condenser being used, until 50 cc. have passed over into the receiver filled with 10 cc. of ammonia solution. This almost corresponds to what the German Pharmacopoeia recommends.

It becomes clear from the investigations of Wehrmann and Wegener that the method of the 5th edition of the German Pharmacopoeia for estimating mustard oil in mustard powder, mustard oil, spirit of mustard and mustard paper affords very good results and is easily carried out. Meyer likewise thinks this method to be the best and the most reliable.

Some years ago we studied the *influence of the rate of saponification on the estimation of the ester value* in linalyl and terpinyl acetates, as well as on bergamot oils to which terpinyl acetate had been added, working out a method for proving the presence of terpinyl acetate which is now in general use[3]). While investigating the speed of saponification of linalyl, terpinyl and geranyl acetates, C. L. Barrillet and R. Berthelé[4]) arrived at the same result as we. They saponified the esters, which had previously been purified by fractionation, at the temperature of the water-bath as well as at 15 and 0°. On boiling, the linalyl acetate was completely saponified after 10 minutes, terpinyl acetate only after 1 hour. It further resulted that at 15° 16.9 p.c. of the linalyl acetate, 1.9 p.c. of the terpinyl acetate and 71.2 p.c. of the geranyl acetate had been saponified. The numbers were after 4 hours: 43.1, 8.4 and 86.8; after 15 hours: 74.4, 24.1 and 88.2, and after 48 hours: 84.2, 49.6 and 88.2 p.c., whereas after 3 hours' boiling the percentages established were: 85.5, 92.1 and 88.2. Consequently, geranyl acetate is the most easily saponifiable. Of terpinyl acetate, 53.5 p.c. after 3 days, 62.7 p.c. after 4 days, 71.2 p.c. after 5 days, 77 p.c. after 6 days and 83.6 p.c. after 7 days were found to have been reacted upon (temperature 13 to 14°).

Further, mixtures of linalyl and terpinyl acetates as well as of bergamot oil with terpinyl and linalyl acetates were saponified for 3 hours in the heat, and for 24 hours at room temperature (15 to 16°). The difference between the figures thus obtained corresponds to the quantities of terpinyl acetate contained in the mixtures. For pure

[1]) *Journ. de Pharm. et Chim.* VII. **6** (1912), 160. — [2]) Comp. *Report* April **1909**, 102. — [3]) *Reports* October **1910**, 60; October **1911**, 116. — [4]) *Bull. Soc. chim.* IV. **17** (1915), 20.

linalyl acetate, after a saponification of 3 hours in the heat and of 24 hours at room temperature, contents of 85.5 and 80.3 p.c. were found: difference = 5.2. The differences were: 15.7 p.c. for a mixture of 75 p.c. of linalyl acetate and 25 p.c. of terpinyl acetate, 30.1 p.c. for the proportion 1:1, 46.4 p.c. for 1:3 and 59.5 p.c. for pure terpinyl acetate. Bergamot oil and a mixture of bergamot oil with orange oil terpenes and linalyl acetate did not show any difference when treated in the same manner in the heat or in the cold; but when a mixture of 70 p.c. of bergamot oil, 20 p.c. of orange oil terpenes and 10 p.c. of terpinyl acetate was used, the difference amounted to 4.6 p.c. The differences became still more noticeable at 0°. The quantity of potash lye and its concentration likewise influence the result of the saponification. Thus 25 cc. of N/2 potash lye saponified, in 48 hours at 14 to 15°, 84.2 p.c. of linalyl acetate and 49.6 p.c. of terpinyl acetate, but 250 cc. of N/10 potash lye only 39.2 and 10.4 p.c., respectively.

For the determination of terpinyl acetate in linalyl acetate or adulterated bergamot oil, the authors suggest to heat in each case 1.5 g. of the ester with 25 cc. of alcoholic N/2 potash lye for 3 hours and then let the mixtures stand for 24 hours at 15 to 16°.

In the case of adulterated bergamot oils the results are more exact. The saponification of normal bergamot oils with 35 to 40 p.c. of linalyl acetate at 15° is completed in 24 hours. A difference of more than 1 p.c. in the results of saponification points to an adulteration with terpinyl acetate, but the quantity of the adulterant cannot be established exactly in this way.

Of the experiments mentioned are specially interesting only those referring to the saponification of linalyl acetate and geranyl acetate at room temperature, for it results that the rate of saponification in the presence of alcohol is considerably higher for geranyl acetate than for linalyl acetate, which was not to be expected from the outset. This is probably due to that the alkali does not act direct on the original ester, but on the ethyl acetate formed intermediately[1]), and that this change takes place more quickly with geranyl acetate than with linalyl acetate.

We do not see, however, any reason for modifying the method recommended by us for the detection of terpinyl acetate, for it is easily carried out and has proved to be good in the course of years. There are no advantages connected with the proposal of Barillet and Berthelé, the process recommended by them taking far more time without giving any better results than ours. For instance, we found by means of our method of fractional saponification a difference of 19[2]), corresponding to 6.65 p.c. of ester, in bergamot oil to which 10 p.c. of terpinyl acetate had been added, whereas the French authors stated a difference of only 4.6 p.c., when examining after their own method the mixture of 70 p.c. of oil of bergamot, 20 p.c. of orange oil terpenes and 10 p.c. of terpinyl acetate, previously mentioned.

Quantitative determination of hydrocyanic acid.

When examining parts of plants for their content of hydrocyanic acid, one generally has to deal with extremely small quantities of this acid. The analytical methods with the aid of silver nitrate usually fail in this case, as the aqueous distillates nearly always contain reducing compounds in addition to the hydrocyanic acid. Qualitatively, the acid is determined through the Prussian blue reaction, which may likewise be used for the

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[1]) Comp. A. Béhal, *Bull. Soc. chim.* IV. **15** (1914), 565; *Report* April **1915**, 68. — [2]) *Report* October **1911**, 117.

quantitative proof, as A. Viehoever and C. O. Johns [1]) have found. For this purpose, they added sodium hydroxide to the distillate containing hydrocyanic acid (it must contain about 1 to 2 mg.), until its reaction becomes slightly alkaline, and concentrated the solution, which had been placed into a round distilling flask of 200 c.c., by distilling the water over *in vacuo*, the flask being put during the process into a water-bath heated to about 70°. The flask must be provided with a similar condenser as used for the determination of nitrogen according to Kjeldahl. After the liquid has been boiled down to 1 cc., 0.2 to 0.5 cc. of freshly prepared 3 p.c. ferrous sulphate solution and about 0.05 g. of potassium fluoride are added, and the flask is evacuated. From 5 to 10 minutes later the mixture is acidulated with nitric acid of 30 p.c., when the blue colour appears immediately. If only traces of prussic acid are present it is necessary to heat to 50°. One then dilutes with water until a colour is reached corresponding to that of a standard solution of 1 mg. of potash cyanide in 25 cc.

This method is said to be very suitable too for the qualitative determination of prussic acid, as it allows to ascertain quantities down to about 0.00001 g.

The *evaluation of aniseed oil in liqueurs* has been discussed on page 7 of this *Report*.

As to the *quantitative determination of cineol*, see page 17 of this *Report*.

The *use of mercuric acetate* for the investigation of terpenes in essential oil is described on page 77.

Physical Notes.

Relations between optical behaviour and constitution.

We have repeatedly had an opportunity of reporting on the interesting spectrochemical investigations of K. von Auwers and his collaborators [2]). Now again a voluminous publication by von Auwers [3]) on his latest investigations in the spectrochemical domain has made its appearence. We need not here enter into details about the important theoretical considerations regarding the spectrochemical influence of the local isomerism in aromatic aldehydes, ketones and esters, nor about the spectrochemical relations between aromatic hydroxy-aldehydes, hydroxy-ketones and hydroxy-esters and their ethers. The rule is that in aromatic aldehydes, ketones and esters a methyl group in ortho position does not alter the exaltations of the mother substance; almost the same holds good for a methyl group in meta position. A methyl group in para situation, however, seems to increase the optical exaltation regularly. The rule previously established, that aldehydes show higher exaltations than the corresponding ketones and esters, finds confirmation also in the homologues.

It further resulted that methyl takes a special place among the alkyles in that its disturbing action is somewhat smaller than that of its homologues. In consequence the exaltations of homologue ketones come near those of the acid esters in such a degree that the differences, which generally are very small for the methyl ketones too, disappear for practical considerations. The action of methoxyl is considerably stronger than that of methyl. In the case of methoxyl the influence is very pronounced also in meta and ortho positions, above all in the dispersion values. The para derivatives of the methoxyl compounds likewise take a special place, in that they again show higher exaltations.

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[1]) *Journ. Americ. chem. Soc.* **37** (1915), 601. — [2]) Comp. *Reports* October **1910**, 164; October **1911**, 122; April **1912**, 158; October **1913**, 124. — [3]) *Liebigs Annalen* **409** (1915), 212.

In the experimental part of the paper we find the constants of some bodies that come into consideration for our special domain, viz., those of salicylaldehyde, anisaldehyde, methyl and ethyl salicylates.

When investigating a new range of alkyl and aryl derivatives of methylenecamphor for their optical behaviour, H. Rupe[1]) was able to confirm, as had previously been established, that certain laws rule the influence of some groups on the rotatory power. On comparing the rotatory dispersive power of the compounds of the methylenecamphor group, some hydrocarbons derived from citronellal[2]), and a number of menthol and myrtenol esters, he further found that $[\alpha]_F - [\alpha]_C = \text{const.}$ for homologous compounds. This constant may be written as function of the wave-length, in a formula ascertained by Hagenbach[3]). In this way the "characteristic wave-length" is obtained for the corresponding range of compounds, and it has proved to be a useful auxiliary for estimating the dispersion curves. Availing himself of the characteristic wave-length, Rupe established the term of "relative anomalous rotatory dispersion". Some of the compounds prepared by Rupe have such a dispersion.

In the ninth publication by J. Kenyon and R. H. Pickard[4]) on the investigation on the dependence of rotatory power on chemical constitution, entitled, "The co-ordination of the rotatory powers of menthyl compounds, of the menthones and of the borneols", the constants or the optical behaviour of numerous derivatives of these terpene bodies are described. Among others, the following were examined: d,l-menthyl oxalate, and numerous l-menthyl esters of substituted benzoic acids, l-menthyl hydrogen succinate, l-menthyl 2-methoxynaphthoate, l-menthyl phenylcarbamate, di-l-menthyl sulphite, and a great number of ureas and derivatives of carbamic acid.

On account of observations of the rotatory powers, refractivities and molecular solution-volumes of borneol, cinchonicine and benzoyl cinchonicine in certain solvents, D. H. Peacock[5]) arrives at the conclusion that modifications of $[\alpha]$ according to concentration are not caused by changes of the active molecules, but by alteration of the speed of light rays in the solvent. As regards the theoretical considerations which bring the author to this idea, we must refer to the original.

Having continued former investigations, W. P. Jorissen and J. A. Vollgraff[6]) report on the electric conductivity of mixtures of oxygen and autoxidising vapours of benzaldehyde and pinene. They this time used oxygen from the air and increased the surface of vaporization. The vaporization was accelerated by keeping the oxygen in motion along the surface of the liquid, a uviol lamp being employed for irradiation. The authors found that under the influence of irradiation the autoxidation of both compounds increases the electric conductivity of oxygen. The electric conductivity of carbon dioxide is not increased by the presence of benzaldehyde or pinene.

Re *polymerization* of *styrene* see p. 78.

As to the *products obtained from citronellal* through exposure to the light, see p. 81.

[1]) *Liebigs Annalen* **409** (1915), 327. — [2]) Comp. *Report* April **1914**, 136. — [3]) *Zeitschr. f. physik. Chem.* **89** (1915), 582. — [4]) *Journ. chem. Soc.* **107** (1915), 35. — [5]) *Ibidem* **105** (1914), 2782. — [6]) *Chem. Weekblad* **12** (1915), 93; *Chem. Zentralbl.* **1915**, I. 1049. See likewise *Ibidem* **1906**, II. 295.

Botanical Notes.

Wisconsin medicinal plants.

On page 22 of the *Bulletin of the University of Wisconsin,* ser. nº 738, gen. ser. nº 542, Madison 1914, R. H. Denniston and R. E. Kremers publish a list of medicinal plants that grow wild or are cultivated in Wisconsin. No less than 259 species are mentioned, some of which are not officinal any longer.

Dipterocarpus woods.

The genera *Dipterocarpus* and *Shorea* of the N. O. *Dipterocarpaceae,* which furnish gurjun balsam and dammar resin, preponderate in some tropical woods, which then are called dipterocarpus woods. Such woods occur in northern British India, Ceylon, Burmah, Indo-China, the Malay Peninsula, Sumatra, Java, Borneo and right up to the Philippines. They are presumably likewise to be found on Celebes and in New Guinea. W. H. Brown and D. M. Mathews [1]) have published an extensive study on Philippine dipterocarpus woods, in which the distribution of such woods on the Philippines, their economical importance and their botanical composition are discussed. They supply considerable quantities of timber without any great costs, provided that the trees are felled judiciously. Otherwise it might be that there could not be any fresh growth of dipterocarpus, smaller trees of less value taking their place, or even that the woods were turned into desert grass lands. It seems to be difficult to plant dipterocarpus trees, success being obtained only under uncommonly favourable conditions.

The authors do not say anything with regard to the balsam production; they mention the following balsamiferous trees: *Dipterocarpus grandiflorus,* Blanco, *D. tuberculatus,* Roxb. and *D. vernicifluus,* Blanco, as well as the aromatic plants specified hereafter: *Acacia farnesiana,* Willd., *Blumea balsamifera,* DC., *Canangium odoratum,* Baill., *Canarium luzonicum,* A. Gray, *C. villosum,* F. Vill., *Cinnamomum Mercadoi,* Vid., *Citrus Hystrix,* DC. and *Clausena anisum-olens,* Merr.

Fungus diseases of essential oil plants.

E. M. Holmes [2]) gives a review of the fungus diseases affecting the plants yielding essential oils.

The North American *Abies balsamea,* Mill., which yields Canada balsam, suffers from the attacks of a fungus belonging to the *Ascomycetes* and known as *Dasyscypha calycina,* Fuchel, or Larch canker. This fungus, which has also been called *Peziza Willkommii,* Hartig, is a wound parasite and may occur wherever the tree trunk is injured. It forms small orange-red discs, surrounded by white hairs. An allied species, *Dasyscypha resinaria,* Rehm., likewise attacks *Abies balsamea. D. calycina* also attacks *Pinus sylvestris,* Linn., *Pinus Pumilio,* Haenke, and *Abies sibirica,* Ledeb. On the leaves of *Abies balsamea, Calyptospora (Pucciniastrum) Goeppertiana,* Kühn *(Melampsoraceae)* is to be found. Its teleutospores occur on species of *Vaccinium* (cranberries). Diseased *Vaccinium* plants should, therefore, be destroyed and burnt wherever the *Abies balsamea* grows.

Plasmopara nivea, Schröt., appears on the under side of the leaves of angelica as a delicate white mildew. The mycelium is permanent in the roots of some of the host plants, but does not seem to affect the percentage of volatile oil yielded by the root.

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[1]) *Philippine Journ. of Sc.* **9** (1914), A. 413, 517. — [2]) *Perfum. Record* **5** (1914), 411, 432.

Celery suffers from various fungus diseases. One of the most troublesome, known as "celery leaf scorch" or "celery rust", is caused by *Septoria Petroselini* var. *Apii (Sphaerioideaceae)*. It appears first in the form of small scattered pale green spots, subsequently increasing in size until the leaf is covered, which then turns brown, curls up and withers; in this state the disease is called "celery blight". Finally, the perithecia appear as tiny black spots. If discovered in an early stage, the disease may be subdued with potash sulphide; all the foliage with perithecia should be burnt. Another disease, known as "celery leaf rot", is due to *Sclerotinia sclerotiorum,* Mass. It attacks the roots and causes the heart of the plant to become pulpy, and ultimately kills the plant. As this fungus passes through the winter in the sclerotia stage, all dead portions of the celery should be burnt where the disease is prevalent. *Puccinia bullata,* Winter, also occurs on celery, as well as on dill and parsley, but is not serious unless present in quantity.

A disease attacks seedling cloves, and will also kill trees 12 to 14 feet high, but it has not been thoroughly investigated. The fungus causing it apparently belongs to the Peronospora group. There is also a disease attacking the rhizomes of the ginger plant, but it has not as yet been accurately described.

The leaves of Iris and Freesia species are subject to the attacks of *Heterosporium gracile,* Sacc. *(Dematiaceae).* The leaves wither early and die. *Puccinia iridis,* DC., is likewise pernicious on iris. *Mystrosporium adustum,* Mass. *(Dematiaceae)* destroys sometimes the bulbs of *Iris reticulata.* It is said that soaking the bulbs for two hours in a solution of 1 part of formalin in 300 parts of water will kill the fungus without injuring the bulb. The disease is styled "iris bulb scab". "Iris rot" is due to *Bacillus omnivorus, Pseudomonas viridis, P. fluorescens* and *P. exitiosus.* The portion immediately below the ground becomes soft and rotten, and the disease often extends to the rhizomes and the offshoots. The presence of the disease is indicated by the wilting of the leaves, which soon become yellow and die. As soon as this is the case, the plants must be dug out and burnt. Superphosphate of lime is said to check the disease, whilst quicklime favours its development.

The roots of the juniper shrubs are destroyed by "conifer root rot" *(Fomes annosus,* Fries, *Polyporaceae),* whereas *Gymnosporangium juniperinum,* Wint. *(Pucciniaceae),* grows exuberantly on the stem and the branches. The aecidia of the fungus grow on the mountain ash. Juniper is likewise attacked by *G. clavariaeforme,* Jacq. (aecidia on hawthorn and *Sorbus Aria*), and *G. Sabinae,* Wint. (aecidia on pear tree leaves). The latter also lives on *Juniperus Oxycedrus,* L., *J. virginiana,* L., and *J. phoenicea,* L. The removal of the host plants from the near neighbourhood of juniper will stop the disease. *Keithia tetraspora,* Sacc. *(Phacidiaceae),* is also found on juniper needles, but it has not been regarded as a serious pest.

The lemon and orange trees are exposed to several fungus diseases. *Colletotrichum gloeosporioides,* Penzig *(Melanconiaceae),* causes a destructive disease on lemon, lime and orange trees. The tips and edges of young leaves are first attacked, becoming light green, and eventually brown, or nearly black, little heaps of spores being formed on both sides of the leaf. The leaf withers and the young shoots shrivel. The blossoms are also attacked and the young fruits then fall very easily, so that often no single fruit remains on the tree. Fruits can be infected if their surface is abraded, when the disease often develops after they have been shipped. They then are of no value at all. It has been recommended to wash the fruit after gathering with potassium sulphide or ammoniacal solution of copper carbonate. Possibly formaldehyde would be better on account of its leaving no deposit. All diseased twigs and leaves should be burnt.

The disease is known as "canker lemon spot", „leaf spot", "wither tip", or "anthracnose". Another danger for lemon trees is *Cladosporium citri,* B. et F., called "lemon scab". It roughens the leaves by raised corky growths on the upper surface. When the fruit is attacked its market value is lowered. *Capnodium citricolum,* M'Alpine *(Perisporiaceae),* covers leaves, stems and fruits with a sooty mould. It grows on the honey dew exuded by insects, the best remedy being to destroy the insects by spraying.

The "lemon fruit rot" is due to various *Penicillium* species, especially *P. italicum,* Wehmer, and *P. glaucum,* Link. *(Aspergillaceae).* But these are saprophytic, and the fruit rarely rots, unless the spores get into it where the skin or cuticle has been broken by careless handling.

The "brown fruit rot", caused by *Pithyacistis citrophora,* R. E. Smith, has brought about severe losses in California. It first appears as a brownish or purplish discolouration of the rind and is characterized by a peculiar odour, which attracts small flies; it spreads readily from fruit to fruit. Remedies suggested are formalin, potassium permanganate or copper sulphate.

The causes of the disease called "dieback", characterized by the dying-back of the leaf tips, rusty spots on the leaves and twigs, the formation of gum and the falling of the small fruit, is not known as yet exactly. It has been suggested that *Agaricus citri* and *A. hesperidum* have some connection with the formation of the gum, these fungi being saprophytic on decaying roots.

Polyporus obliquus and *P. fumosus* have been found to attack the roots through wounds, and kill the trees in from three to five years. These fungi and also *Rhizoctonia violacea* are said to be destructive in Malta to citrus trees grown in clay soil on low ground. In order to sterilize soil containing *Rhizoctonia,* carbolic acid is recommended.

A disease known as the "black rot" has been reported from South Africa, due to *Diplodia natalensis,* appearing first as a translucency of the rind at the stalk end of the fruit, the tissue rapidly softening and becoming brown, and the colour spreading over the whole fruit, which becomes ultimately black, with a shrivelled surface.

Phytophthora Syringae, Kleb. *(Peronosporaceae)* lives as a parasite on lilac and destroys its buds and twigs. *Phyllosticta Syringae,* Westend. *(Sphaerioidaceae),* likewise becomes injurious on lilac.

Mignonette has to suffer from *Cercospora Resedae,* Fuck. *(Dematiaceae),* the leaves showing brown spots. Spraying with dilute Bordeaux mixture, as soon as the disease is noticed, is recommended.

Narcissus leaves are attacked by *Puccinia Schroeteri.* The bulbs of non-odorous narcissus species show to a serious extent a disease caused by *Fusarium bulbigenum,* Cooke et Mass. *(Tuberculariaceae),* the presence of which is first indicated by small yellowish spots on the leaves. The mycelium of the fungus passes down the tissue of the leaf into the basal portion from which the scales arise, and the whole of the scales are attacked. The bulbs then become attacked by saprophytic fungi, such as *Penicillium.*

Two fungus diseases have been reported as attacking the nutmeg tree. One attacking the bark has been named *Eutypa erumpens,* Massee *(Valsaceae),* and has occurred in Barbados, Grenada and Trinidad. The other, *Corticium javanicum,* Zimm., has been reported from Java. It attacks the roots.

The "gum disease", "mal di gomma", of the orange tree is perhaps due to *Fusarium limonis,* Briozi, or *Agaricus citri,* but it may be that it is due to bacteria. *Cladosporium herbarum,* Lk., var. *citricolum,* Lk., affects the bark of the tree as well as the rind of the orange. It has been identified with the conidial form of *Sphaerella*

Tulasnei. Cracks are caused by it, through which *Colletotrichum gloeosporioides* (see before) enters and causes the death of the parts affected. Spraying with Bordeaux mixture is recommended.

"Melanose" is another disease of the orange which has been reported from Florida, Cuba and Australia. It occurs on the leaves, fruit, and twigs, forming brownish-black elongated spots. The leaves fall rapidly, and the trees consequently cannot thrive. The fungus causing it has not been determined so far.

Gloeosporium Pelargonii, Cke. et Mass., is known to attack pelargonium plants, but it does not seem to have been recorded as injurious to the scented species. It forms minute spots on the under surface of the leaves, which soon drop and wither.

"Mint rust" is well known, as it often destroys whole beds of mint. It is due to *Puccinia Menthae*. The aecidium causes the stem to be swollen and distorted, and to become covered with orange-yellow spots. The summer or uredospores are developed as yellowish spots on the leaves, and the *Puccinia* or winter spores form blackish spots on the leaves. The mycelium of the aecidium stage is perennial in the underground stems, so that when once a plant is affected it can produce the disease every year. In the spring of the year, therefore, all peppermint plants with distorted stems and pale leaves should be dug up and burnt. The disease also affects wild mints and may easily be communicated from them to peppermint. Dry seasons are favourable to the disease.

One of the most dreaded diseases of roses is the „rose mildew", caused by *Sphaerotheca pannosa (Erysibaceae)*. Roses with soft leaves are more subject to it than those with hard, shining leaves. There are two periods of attack, one in the spring, often following a check caused by late frosts, and one soon after midsummer, when the roots are suffering from drought. Spraying with a solution of potassium sulphide or dredging with flowers of sulphur is very effective. "Rose rust", *Phragmidium subcorticium*, Schrank *(Pucciniaceae)*, forms orange-coloured patches of uredospores on the leaves and young shoots; later on the black teleutospores appear on the under surface of the leaves. The leaves that fall in autumn, bearing these black dots, should be burnt, and the plants that have been attacked should be drenched with sulphate of copper solution during the winter. "Rose canker" is due to *Coniothyrium Fuckelii*, Sack. *(Sphaerioidaceae)*, which is considered by some the conidial stage of *Leptosphaeria Coniothyrium*, Sacci. It appears first as reddish patches, scattered over the green bark. Minute cracks then appear, and an increase of cells causes the formation of swellings, on which the pycnides appear as black dots. The fungus is a wound parasite. It is recommended that in the early stage when red patches appear they should be painted with Stockholm tar containing creosote.

Actinonema Rosae, F. *(Sphaerioidaceae)* causes "rose black spot", the mycelium penetrating the whole of the leaf and causing premature falling of the leaves, in consequence of which the buds expand before their time. Fibres radiate from the centre of the circular dark purplish spots which characterize the disease, and black perithecia are attached to the fibres. As soon as the spots appear, the roses should be sprayed with potassium permanganate or potassium sulphide solution; all spotted leaves must be burnt.

Septoria Rosae, Desm. *(Sphaerioidaceae)*, forms minute, yellowish-green patches on the surface of the leaf. They enlarge and change to a pale brown colour, bounded by a dark line. If the leaf is not full-grown, when attacked, the brown patches often fall out, leaving holes. Those that remain in fully-developed leaves become studded with minute black points of spores. It is a difficult disease to get rid of. The bushes

on which is has occurred and the ground underneath them should be thoroughly drenched in winter with a sulphate of copper solution. The disease is called "rose leaf scorch". "Rose black mildew" is rare; it is due to *Peronospora sparsa*, Berk. The fungi are only to be detected with the aid of a powerful lens. Its presence is evidenced by the sudden drooping of young vigorous leaves, and the shoot bearing them becomes limp and dies. Blackish or reddish stains will then be observed, and on these the mildew can be found by the aid of a lens. At present it seems to be confined to roses cultivated in greenhouses.

Puccinia tanaceti, DC. forms brown spots of rust on the leaves of tansy and sunflower. Bordeaux mixture sprayed over the plant has been found to check the disease.

The tuberose has recently been attacked by *Hypochnus filamentosus*, Pat. *(Hypochnaceae)*, forming a mould on the surface of the leaves. It can be checked by a treatment with rose-coloured potassium permanganate solution, to which a little soft soap has been added.

One of the diseases of the vanilla plant is caused by *Calospora Vanillae*, Massee *(Melanconidaceae)*. In the Seychelles it spread to such an extent that the whole industry was threatened, and it has also been reported from Antigua, New Granada, Réunion and Mauritius.

The violet is subject to several fungus diseases. *Ascachyta Violae*, Sacc. *(Sphaerioidaceae)* causes large circular, yellowish or brown patches to appear on the leaves. These spots subsequently become yellowish-white, dry up and fall out, leaving holes. The leaves should be removed as soon as such spots appear. The disease causes much damage and occurs generally where an excess of moisture is present. *Phyllosticta Violae*, Desm. *(Sphaerioidaceae)* causes a similar disease.

"Violet leaf spot", due to *Cercospora Violae*, Sacc. *(Dematiaceae)*, forms pale rond spots visible on both sides of the leaf. It sometimes becomes epidemic on plants grown in frames, when the plants are crowded, and the soil and atmosphere constantly damp. All leaves with pale spots should be removed, and the plants sprayed with Bordeaux mixture. *Alternaria Violae*, Dorsett *(Dematiaceae)* is widely spread in the United States and causes a most destructive disease. It attacks especially plants of rapid, succulent growth. It appears first as yellowish, semi-transparent spots on the leaves, these spots become blackish and fall out, leaving holes. Clusters of olive-coloured conidia appear on the spots and afterwards spread the disease. "Violet rust", caused by *Puccinia Violae*, DC., occurs on wild as well as on cultivated violets. Spraying with potassium sulphide solution seems to check the disease.

On the leaves of wormwood, a kind of rust caused by *Puccinia Absinthii*, DC., forms small scattered or clustered yellowish or pale brown spots. The teleutospores form in the autumn scattered or clustered round blackish spots on both sides of the leaf and on the stem. Wormwood is attacked, besides, by *Erysiphe cichoracearum*, DC. *(Erysibaceae)*, which also occurs on numerous other plants belonging to different natural orders.

In an additional article, Holmes deals with the application of the different fungicides.

As to *Origanum Bevani nov. spec.*, see p. 29.

Phyto-physiological Notes.

The formation of benzaldehyde by tyrosinase.

If tyrosinase, an oxidase occurring in various plants, e. g. in some fungi, acts on phenyl glycocoll in the presence of cresol, a strong smell of benzaldehyde becomes

noticeable after 12 hours, and the presence of ammonia can easily be proved, as we gather from a paper by R. Chodat and K. Schweizer[1]). The following reaction has, therefore, taken place: separation of carbon dioxide and ammonia, and oxidation to the aldehyde containing one carbon atom less. The presence of formaldehyde in green plants might, in consequence, likewise be due to the action of the always-present tyrosinase, this forming formaldehyde from glycocoll, when the chlorophyll might foster the process. In fact, the quantity of formaldehyde formed from glycocoll by the action of tyrosinase is increased in the presence of chlorophyll solution.

G. Bertrand and A. Compton[2]) have investigated the changes which take place with age in amygdalinase and amygdalase. These enzymes show the maximum activity in a medium reacting distinctly alkaline on phenolphthalein. In the course of time (2 to 4 years), they not only lose their efficacy very slowly, but they require, besides, as optimum an ever-increasing concentration of the hydrogen ions.

The *reduction of cinnamaldehyde by yeast* is discussed on page 82 of this *Report*.

Pharmaco-physiological Notes.

Remedies against vermin.

On page 74 of our previous *Report* we talked about the different remedies which have, of late, been recommended against vermin. The literature on the lice pest has meanwhile become quite voluminous, and we have before us numerous communications[3]) which evidence the importance of essential oils for checking the lice pest. The opinions concerning the efficacy of essential oils are, of course, divided. According to Zucker, they range as follows: gaultheria oil, camphor oil, bergamot oil, eucalyptus oil, rosemary oil. Their influence is destructive only after a comparatively long action, and Fränkel says that the good results obtained are probably to be attributed to the fact that body lice evade the smell of essential oils and of their components. Wulker ascribes the greatest efficacy to eucalyptus and clove oils. Von Knaffl-Lenz found that cineol ointment killed lice in 4 to 6 hours, whereas anisole ointment proved ineffective. Blau recommends methyl salicylate, which combines preventive and destructive actions and does not harm the human organism. Its application is simple and it can be procured at little cost.

Rabe thinks that the success obtained with certain volatile oils, such as aniseed, fennel, clove, eucalyptus, thyme oils and others, in the form of ointments against lice, is due to their content of terpenes[4]). He examined from this point of view the effect

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[1]) *Arch. Sc. phys. et nat. Genève* (4) **39** (1915), 331; *Chem. Zentralbl.* **1915**, II. 194. — [2]) *Compt. rend.* **159** (1914), 434; *Chem. Zentralbl.* **1915**, I. 1068. — [3]) T. von Marschalkó, *Deutsche med. Wochenschr.* **41** (1915), 316; *Chem. Zentralbl.* **1915**, I. 1329. — F. Rabe, *Apotheker Ztg.* **30** (1915), 398. — A. Zucker, *Centralbl. f. Bakteriol., Parasitenk. u. Infektionskrankh.* **76** (1915), 294; *Apotheker Ztg.* **30** (1915), 399. — G. Wulker, *Münch. med. Wochenschr.* **62** (1915), 628; *Chem. Zentralbl.* **1915**, II. 418. — E. v. Knaffl-Lenz, *Wien. klin. Wochenschr.* **28** (1915), 708; *Chem. Zentralbl.* **1915**, II. 419. — H. Blau, *Zeitschr. d. allg. österr. Apoth. Ver.* **53** (1915), 171. — S. Fränkel, *Therap. Monatsh.* **29** (1915), 301. — *Zeitschr. d. allg. österr. Apoth. Ver.* **53** (1915), 137. — B. Nocht and J. Halberkann, *Münch. med. Wochenschr.* **62** (1915), 626; *Chem. Zentralbl.* **1915**, II. 417. — Hönck, *Deutsche med. Wochenschr.* **1915**, 368; *Therap. Monatsh.* **29** (1915), 282. A review of several papers is given by Th. Sutter, *Deutsche Parf.-Ztg.* **1** (1915), 71. — [4]) Aniseed and fennel oils, however, contain scarcely any terpenes or none at all.

of volatile oils with high oxygen and terpene contents on insects and found that flies, gnats, butterflies, moths, spiders and leaf lice were quickly asphyxiated by turpentine oil and pine tar oil vapours. The author had no body lice at hand, but he thinks that they would die at least as quickly as leaf lice. Rabe sees an explanation of the quick killing action of turpentine oil in that the terpene vapours absorb the oxygen of the surrounding air, thus creating an atmosphere lacking in oxygen, in which the insects are suffocated. In this we cannot share the author's opinion, but rather believe in a toxic action of turpentine oil, as long as it has not been proved by experiments that lice perish quickly in an atmosphere devoid of oxygen. Marschalko's observation that lice perish within from 10 to 15 minutes in a test tube, into which a small drop of turpentine oil has been put under cotton wool, agrees with Rabe's conjecture.

Incitement of the smelling organs through aromatics.

Weiss[1]) states, in an article recently published, on the olfactive organ and its development, that aromatics incite the smelling organs by their chemical action[2]). They must be gaseous, the mucous membranes of the nose must be moist, and a current of air must pass over them. The more intense the current of air, the more distinct the perception of odour. When keeping the breath or respiring through the mouth there is no such perception. Some substances still act in very considerable dilution, e. g. bromine $\frac{1}{30\,000}$, musk $\frac{1}{200\,000}$, chlorophenol $\frac{1}{4\,600\,000}$, mercaptane $\frac{1}{460\,000\,000}$, iodoform $\frac{1}{10\,000\,000\,000}$ mg. per 1 cc. of air. Sharp and pungent smells (chlorine, acetic acid) do not affect the olfactive sense, but that of touch.

Acuteness of the smelling power of the dog.

In the perception of most of the pure aromatics the human being outrivals the dog, whereas the dog is far ahead of man when mixtures of aromatics of animal origin are concerned, as L. Seffrin[3]) has found out by experiments. The smallest quantities perceived by the dog were: ether = 0.001 to 0.0009; methyl salicylate = 0.0033 to 0.0028; formaldehyde = 0.002 to 0.001; anisaldehyde = 0.0006 to 0.0005; xylene = 0.00055 to 0.0005; urine of a she-dog = 0.025 to 0.05 and expressed beef juice = 0.0025 to 0.002 g.

It is not mentioned in the abstract, how the experiments were carried out but the reader is referred to the original.

Use of artificial camphor for therapeutical purposes.

During the period which this *Report* covers, it has been reported again from various quarters on the use of artificial camphor in medical practice[4]). In general, the results are very favourable and it seems that artificial camphor can perfectly replace the genuine article in therapeutics. Bachem experimented with animals, whereas Levy and Wolff report on clinical experiments, when the entire camphor action was obtained with the artificial product. Unpleasant by-effects were not noticed. Lutz made similar favourable experiences.

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[1]) *Deutsche Parf.-Ztg.* **1** (1915), 77. — [2]) Comp. Teudt, who explains the manifestations of the sense of smell by assuming them to be due to the oscillations of electrones within the molecules or atoms. *Report* April **1914**, 123. — [3]) *Zeitschr. f. Biologie* **65** (1915), 493; *Chem. Zentralbl.* **1915**, II. 416. — [4]) C. Bachem, *Med. Klinik* **1915**, 425; *Apotheker Ztg.* **30** (1915), 214. — M. Levy und W. Wolff, *Ther. d. Gegenw.* **1915**, 88; *Therap. Monatsh.* **29** (1915), 262. — C. Lutz, *Berl. klin. Wochenschr.* **52** (1915), 322; *Chem. Zentralbl.* **1915**, I. 1329. Comp. *Report* April **1915**, 76.

Copaiba balsam and copaiba balsam oil with reference to gonorrhoea.

R. Stockman[1]) deals with the action of copaiba balsam and copaiba balsam oil on gonorrhoea. He asserts that the balsam has scarcely any influence on the disease, but that the oil possesses healing properties.

Turpentine oil in the treatment of wounds.

As L. Lematte states[2]), turpentine oil is a valuable aid in the treatment of wounds. It is used especially as a tincture and as a serum[3]). The tincture is prepared by dissolving 0.1 g. of magenta in 10 g. of turpentine oil, to which solution 10 g. of alcohol of 95 p. c. and 10 g. of ether are added. In order to make the serum, 1.5 g. of turpentine oil are triturated in a mortar with 8 g. of sodium chloride, and boiled water is then added gradually to make 1 litre. On arrival of the patient at the hospital, a purulent wound is first treated for 15 minutes with an undiluted hydrogen peroxide, twelve volumes. Then it is washed out with a mixture of equal parts of hydrogen peroxide and the turpentine serum and dried with sterile compresses. All mortified tissue is removed with scissors and forceps, the cleaned wounds swabbed out with cotton tampons soaked in the tincture, so as to penetrate all the tissue. It is allowed to dry for several minutes, then covered with a compress of absorbent cotton soaked in the serum. No impermeable material should be used for covering this. The bandage is renewed daily, and the tincture is put on all the pale-looking places. The healthy tissue is of blood-red colour and needs only the dressing with serum. If the healing does not progress, the tincture is again used. The cicatrizing and antiseptic power of the tincture are far greater than those of iodine tincture, and its cost is negligible. For all surgical lavations, the serum is to be preferred to sterile water, as the hypertonicity of this delays the healing process. Fistulous wounds may be treated with strips of gauze soaked with the tincture. This liquid has the slight disadvantage of staining skin and linen. The stains should be rubbed with a sublimate solution (1:1000). Seriously infected limbs, which endangered the patient's life, have been saved from amputation through this treatment.

Therapeutical use of pinene ozonide.

Oil of turpentine is an old sterling remedy against all affections of the respiratory organs, but has the disagreeable property to irritate the kidneys, when given in large doses. This is said not to be the case with pinene monozonide, or oxypinene, as B. H. Waters[4]) calls the preparation. It does not harm the kidneys at all. It possesses all the valuable therapeutic qualities of pinene, acts, however, generally in a milder form, and is said to be of good service in the treatment of consumption. It is reported to act as expectorant in cases of dry, ineffectual cough and to cause in general a more abundant secretion of the glands, just the same as turpentine oil. In addition, it seems to stimulate both appetite and digestion.

Pinene monozonide is formed by the action of dry ozonized air on pinene vapours.

With reference to this we beg to mention the process worked out by A. S. Ramage[5]) for the oxidation of terpene compounds and the production of terpene peroxide. It is an improvement on the U. S. Pat. 710893 of the same inventor, and consists in

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[1]) *British Medical Journal* **1915**, 11, 128; *Chemist and Druggist* **87** (1915), 156. — [2]) *J. Med. Chirurg. Pract.; L'Union Pharm.* **56** (1915), 229. As per *Pharmaceutical Journ.* **94** (1915), 801. — [3]) The name of serum is here used for a kind of physiological salt solution. — [4]) *Americ. Journ. Pharm.* **87** (1915), 163; *Pharmaceutical Journ.* **94** (1915), 767. — [5]) U. St. Pat. 1097939; *Chem. Ztg. Repert.* **39** (1915), 104.

that the cineol vapours, heated to over 100°, are exposed to the influence of ozone or ozonized air in the presence of a catalyst, with preference platinum-black. The terpene vapours are oxidized more quickly in consequence, whilst the cascade-like arrangement of the receivers of the peroxide facilitates the separation of the compound. The same author has taken out patents for the manufacture of an organic peroxide and of terpene oxide[1]). When ozone acts on cineol at room temperature, in the presence of platinum-black, a viscid, thick, non-volatile neutral syrup of brownish-yellow colour results. This body of unknown composition is an organic peroxide which easily gives off to water eighteen times its volume of loosely connected oxygen. It is readily miscible with heavy mineral oils or melted vanillin and is a valuable disinfecting agent, which produces a cooling sensation on the skin.

If anhydrous pure cineol is brought together with an oxidizing anhydrous body, such as ozone or ozonized air, and heated to about 60°, approximately half of the cineol is transformed into a higher oxide of the formula $C_{10}H_{18}O_2$. This peroxide decomposes with water into a terpene and hydrogen peroxide. It is meant for the disinfection of wounds, for respiration in cases of advanced consumption, and for disinfection of the air by spraying.

Urinod, the cause of the characteristic odour of urine.

It is a well known phenomenon that the urine of a person to whom turpentine oil has been administered takes the smell of violets, but so far no explanation has been found for this. Until a short while ago, it was still unknown to what bodies urine owes its peculiar odour. It cannot be caused by the volatile substances present (formic, acetic, propionic, butyric and benzoic acids, ammonia, methylamine, indole, scatole, phenol, *p*-cresol, &c.). W. M. Dehn and F. A. Hartman[2]) have now found that the smelling principle of urine is a substance, C_6H_8O, volatile with steam, which they call urinod. It is probably identical with 3-cyclohexenone-1. Urinod does not occur free in the urine, but in the conjugated form, being liberated by fermentation or by the action of dilute sulphuric acid. It boils at 108° (28 mm.), has a penetrating, clinging, nauseous smell and is very poisonous. One drop of urinod put on filter paper will still smell after 15 months. It yields a dinitro compound melting at 78° and a semicarbazone melting at 254°. In order to prepare urinod, sulphuric acid is added to urine in the proportion of 3:100, the mixture allowed to stand for several days, and then distilled. Out of 1000 litres of urine 5.18 g. of urinod were obtained.

As to a *case of poisoning through American wormseed oil*, see p. 43.

The *removal of warts* with the aid of *cinnamon oil* is mentioned on p. 14 of this *Report*.

Chemical Notes.

Hydrogenation with nickel and hydrogen at different pressure.

A. Brochet and M. Bauer[3]) report on hydrogenations with the aid of nickel and hydrogen at raised and at ordinary pressure. Cinnamic acid and methyl cinnamate yield, under a pressure of from 8 to 15 kg. per square cm., phenylpropionic acid and

[1]) U. S. Pat. 1097940 and 1098356; *Chem. Ztg. Repert.* **39** (1915), 104. — [2]) *Journ. Americ. chem. Soc.* **36** (1914), 2118, 2136. — [3]) *Bull. Soc. chim.* IV. **15** (1914), 554; **17** (1915), 50, 55. Comp. *Report* April **1915**, 80.

its methyl ester. The reaction is slower at ordinary pressure. Ethyl cinnamate forms ethyl phenylpropionate (b. p. 127° at 15 mm.), if hydrogenated under pressure. The authors obtained *p*-methoxypropylbenzene (b. p. 209 to 211° at 761 mm.) from anethole, dihydroeugenol and octohydroeugenol (phenylurethane, m. p. 272°) from eugenol, dihydrosafrole from safrole, (b. p. 238 to 230°) and dihydroeugenol from *iso*eugenol.

Action of ozone on organic compounds.

C. Harries and his collaborators, as well as other scientists, have shown by their experiments that the ozone method is of great service in determining the constitution of organic compounds[1]). Harries[2]) has now published a summary of the action of ozone on organic compounds, in which he discusses the ozone method in general and reports on his most recent experiences in this realm.

In first place, Harries calls attention to the advantages and disadvantages of the ozone method, prompted to do so by the assertion of a fellow-chemist that it was not by far so applicable as the catalytic reduction method. There is a certain similarity between the two, for in either case, besides hydrogen and oxygen, nothing is introduced that might make the isolation of the reaction products more difficult. Furthermore, wherever a body can be hydrogenated catalytically, ozone derivatives may likewise be obtained from it, but not *vice versa*. All endeavours have failed, for instance, to hydrogenate india-rubber, although the ozonization takes place easily. A serious advantage of the catalytic hydrogenation method consists in its being extremely convenient and cheap, whereas the ozonization apparatus is expensive. In addition, it is more difficult to handle the ozonides, special experiments being necessary for every isolated case. In Harries' opinion, the essential value of the hydrogenation method lies only in that it permits of preparing new bodies direct from the unsaturated compounds, whereas nothing definite is ascertained regarding the position of the double linking. He lays stress on some unconditional advantages of the ozonization method, pointing out that the position of the double linking can easily be ascertained from the character of the ozonides and by isolating their decomposition products. The ozonization method is not only applicable in a more general way, but it penetrates also far deeper into the nature of the compound.

A difficulty, which in the course of time has made itself felt often enough as inconvenient, consists in that certain bodies, such as terpene alcohols and unsaturated phenols, do not yield uniform normal ozonides. However, if very dilute solutions are used and ozone which has previously been washed in a 5 p. c. caustic soda lye and concentrated sulphuric acid, the normal ozonides are obtained in almost every case. Concentrated ozone may split off water from cholesterol and terpineol. From cyclic hydrogenated hydrocarbons, ozonides are sometimes obtained, the composition of which lies between that of the normal ones (O_3) and the oxozonides (O_4). With proper treatment, one now almost invariably succeeds in preparing what is intended, i. e. either the normal ozonide or the oxozonide.

A second difficulty, which has not yet been removed completely, consists in that the decomposition of the ozonides with water and glacial acetic acid may give rise to very stable peroxides of the aldehydes or ketones, the existence of which was altogether unknown before the ozone reaction.

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[1]) Comp. e. g. *Reports* April **1906**, 98; April **1907**, 115; April **1908**, 178; October **1909**, 188; October **1910**, 194; October **1912**, 145. — [2]) *Liebigs Annalen* **410** (1915), 1.

It is very important to decide whether the action of ozone may cause a change in the position of the double linking. The cases where such a transposition is possible are not very numerous. The groups $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!C\!:\!C-$ and $\begin{matrix}CH_3\\CH_2\end{matrix}\!\!>\!C-$, as occurring for instance in rhodinal (IV) and citronellal (I), come chiefly into consideration. The results afforded by the action of aqueous potassium permanganate [1]) on citronellal have but one meaning, as only derivatives of rhodinal are obtained. Intermediate products can only be isolated with the aid of potassium permanganate in acetone. Through the action of ozone, however, products are formed which indicate that the commercial citronellal is a mixture [2]). A content of 40 p. c. of rhodinal can be deduced from the quantities of acetone or acetone peroxide and β-methyladipic acid, as the only decomposition products that could be isolated at the beginning.

Harries continued these investigations together with G. Wagner [3]). He did not allow the ozone to act direct on the aldehyde, as before, but on its dimethylacetal. But even then the decomposition did not lead up to the desired result, as principally only acetone peroxide and β-methyladipic acid could be traced, in addition to a new body, a keto-aldehyde. It became evident from this experiment that in the decomposition of the ozonide of citronellaldimethylacetal by water the acetal groups were split off, so that the aim of protecting the aldehyde group against alterations by acetalizing it had not been gained.

Later on, Harries again tried the problem in company with F. Comberg [4]). As an indifferent product, the peroxide of methyloctanonal (II) was isolated; on being heated with potash lye it passes into ethanoyl-4-methylcyclohexene-1 (III), a cyclic derivative. It was easy to determine the constitution of this compound, as it proved to be identical with the ketone tetrahydro-p-acetotoluene, which Wallach [5]) had prepared synthetically some years before. This tetrahydro-p-acetotoluene can only have formed from the peroxide of the ketoaldehyde (II), which must result from the genuine citronellal by oxidation with ozone.

Whilst in this way the presence of genuine citronellal in the commercial product is proved, on the other hand a series of compounds may be obtained which indicate an admixture of rhodinal. In addition to the β-methyladipic acid previously observed, the authors obtained its half-aldehyde and acetone peroxide, as well as a new acid, which they consider to be 5-methyl*cyclo*pentenecarboxylic acid (V).

It results from these experiments that commercial citronellal is not uniform, with which, however, does not agree the fact that it yields a semicarbazone, described already by Tiemann and Schmidt, and which uniformly melts at 84°. In consequence, one tried to split the semicarbazone into its components by crystallization, but no alteration of the melting point could be stated. However, if the semicarbazone was treated with ozone, an ozonide formed which, on decomposition, yielded two semicarbazones. In addition, formic acid, carbon dioxide and acetone peroxide result. The two semicarbazones were identified as methyloctanonal monosemicarbazone (VI), which corresponds to normal citronellal, and as the semicarbazone of the half-aldehyde of the γ-methyladipic acid, which is derived from rhodinal (VII). The proportion calculated is therefore 60 % of citronellal to 40 % of rhodinal. It might be concluded from the experiment in question that the semicarbazone is an individual substance in which a shifting of the double linking is produced by ozonisation. Harries does not consider

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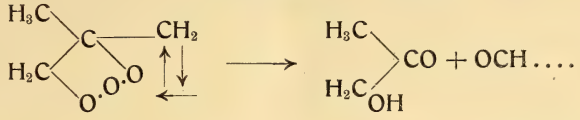
[1]) Tiemann and Schmidt, *Berl. Berichte* **29** (1896), 903; *Report* October **1896**, 88. — [2]) Harries and Himmelmann, *Berl. Berichte* **41** (1908), 2187; *Report* October **1908**, 185. — [3]) *Inaugural-dissertation*, Kiel 1913. — [4]) *Inaugural-dissertation*, Kiel 1914. — [5]) *Liebigs Annalen* **360** (1908), 54.

this supposition as proved, for it is not impossible that the citronellal semicarbazone is a very difficultly separable mixture of two semicarbazones.

A new type of decomposition of ozonides by water was discovered by the isolation of acetylcarbinol, $CH_3 \cdot CO \cdot CH_2OH$, from the products of decomposition of citronellal and citronellol ozonides. This reaction may be explained by supposing that citronellal adds ozone in a normal way and that the following peroxide-like transposition takes place:

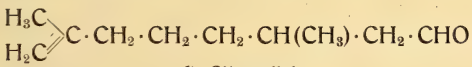


The quantities of acetylcarbinol found were very small. No acetylcarbinol formed in the transposition of the ozonide of citronellalsemicarbazone.

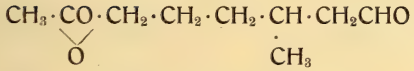
In the experimental part of the paper we find particulars about the preparation and the properties of pinene ozonide. Harries conducted ozone, the ozone content of which had been reduced as far as 9.3 to 4.8 p.c. by washing with a 5 p.c. soda lye and concentrated sulphuric acid, into a solution of pinene from French turpentine oil in hexane, until no more bromine was added, thus obtaining a solid ozonide, $C_{10}H_{16}O_3$, and a syrupy ozonide, which became very frothy in a vacuum. Besides, an oily body of unknown composition had formed. The best yield of solid ozonide was obtained with the aid of a freezing mixture.

*cyclo*Hexene yields a monomeric liquid ozonide of pungent disagreeable odour and a solid polymeric ozonide which explodes violently at about 140 to 150°

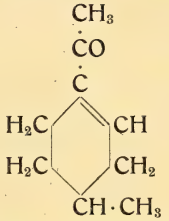
Harries obtained from *cyclo*pentene, in addition to the already known normal, viscid ozonide, an explosive polymeric as well as a non-explosive polymeric ozonide.



(I) Citronellal.



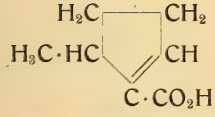
(II) Methyloctanonal peroxide.



(III) Ethanoyl-4-methyl*cyclo*hexene-1.

$(H_3C)_2C:CH \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CHO$

(IV) Rhodinal.



(V) 5-Methyl*cyclo*pentene carboxylic acid.

$CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH:N \cdot NH \cdot CO \cdot NH_2$

(VI) Methyloctanonal monosemicarbazone.

$HO_2C \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH:N \cdot NH \cdot CO \cdot NH_2$

(VII) Semicarbazone of the half-aldehyde of γ-methyladipic acid.

He further made an interesting observation as to the by-products formed in the preparation of *cyclo*pentene. The reduction of *cyclo*pentanone to *cyclo*pentanol, which serves for the preparation of the *cyclo*pentene, takes a different course, according to whether it is carried out with sodium and absolute ether or with sodium and ordinary ether. As the latter always contains alcohol, which with the sodium forms sodium

ethoxide, it leads to components which boil very much higher. The sodium ethoxide acts first condensing on two molecules of *cyclo*pentanone, whilst the hydrogen evolved further reduces the ketone formed to the saturated alcohol. The *cyclo*pentanone was prepared by distilling adipic acid with barium hydroxide. The reduction with the aid of sodium, ordinary ether and water only yields 33.4 p.c. of *cyclo*pentanol. From the high-boiling products of the reaction, *α-cyclo*pentyl*cyclo*pentanol and the pinakone $C_{10}H_{18}O_2$ (m. p. 108°) were isolated. If the former is oxidized with chromic acid it forms *α-cyclo*pentyl*cyclo*pentanone, which with benzaldehyde yields a condensation product, $C_{17}H_{20}O$, melting at from 97 to 98°. According to Wallach's directions[1]), *α-cyclo*pentyl*cyclo*pentanol was converted into *α-cyclo*pentyl*cyclo*pentene, which affords a rather unstable ozonide.

Hydroaromatic compounds with *gem*-dialkyl groups.

Some time ago already, K. von Auwers and E. Lange[2]), in a paper on hydroaromatic alcohols and ketones with a *gem*-dimethyl group, described some bodies related to the terpenes, e. g. 1,1-dimethyl*cyclo*hexanol-4, 1,1-dimethyl*cyclo*hexanone-4, 1,1,4-trimethyl*cyclo*hexanol-4, 1,1-dimethyl*cyclo*hexanol-2, 1,1-dimethyl*cyclo*hexanone-2, 1,1,2-trimethyl*cyclo*hexanol-2, 1,1-dimethyl*cyclo*hexanol-3 and 1,1-dimethyl*cyclo*hexanone-3. The same authors[3]) now publish a second paper on these compounds, reporting on some hydrocarbons, alcohols and ketones with several *gem*-dialkyl groups. The properties of the bodies described in this and in the previous publication are given below in tabulated form.

Of the ten possible isomeric trimethyl*cyclo*hexenes with a *gem*-dimethyl group, the authors have so far prepared the 1,1,4-trimethyl*cyclo*hexene-3 and the 1,1,2-trimethyl*cyclo*hexene-2. On oxidation of the former an oily ketonic acid, $C_9H_{16}O_3$, results as chief product and, besides, an unsaturated ketone, $C_9H_{14}O$. This acid may perhaps be the *ββ*-dimethyl-*δ*-acetylvaleric acid, a compound allied to the geronic and *iso*geronic acids.

Experiments of preparing saturated and unsaturated hydrocarbons from tetraalkylated *cyclo*hexanols always yielded mixtures of inconstant boiling point and from which it was impossible to isolate uniform compounds.

Many of these bodies have previously been described by others, but the constants given below are only those observed by Auwers and Lange.

	b. p.	$d\frac{20°}{4°}$	n_D	m. p.
1,1-dimethyl*cyclo*hexanone-4	72 to 73.4° (14 mm.)	0.932	1.45374 (24.2°)	38 to 40°
1,1,4-trimethyl*cyclo*hexanol-4	75° (11 mm.)	—	—	58°
1,1-dimethyl*cyclo*hexanol-2	77 to 78° (14 mm.)	0.929	1.46521 (24.1°)	—
1,1-dimethyl*cyclo*hexanone-2	172 to 172.5° (757 mm.)	0.915	1.44903 (20.4°)	—
1,1,2-trimethyl*cyclo*hexanol-2	75.8° (16 mm.)	0.926	1.46866 (18.4°)	—
1,1-dimethyl*cyclo*hexanol-3	73 to 74° (8 mm.)	0.909	1.46149 (13.7°)	12°
1,1-dimethyl*cyclo*hexanone-3	54° (8 mm.)	0.906	1.44763 (18.6°)	—
1,1-dimethyl*cyclo*hexanol-4	76.5° (9.5 mm.)	0.925	1.4639 (20°)	—
1,1-dimethyl*cyclo*hexene-3	120 to 122° (750 mm.)	0.804	1.4456 (20°)	—
	119.5 to 121.2° (767 mm.)	0.803	1.44521 (20°)	—
1,1,4-trimethyl*cyclo*hexene-3	140° (ordinary pressure)	0.802 to 0.805	1.4454 to 1.4469 (20°)	—
1,1,2-trimethyl*cyclo*hexene-2	146.2 to 147.2° (767 mm.)	0.822 to 0.826	1.4562 to 1.4566 (20°)	—
1,1,4,4-tetramethyl*cyclo*hexanol-2	201.5 to 203° (745 mm.)	0.901	1.4618 (20°)	53°
1,1,4,4-tetramethyl*cyclo*hexanone-2	190.4° (758 mm.)	0.888	1.4459 (20°)	—
1,1-dimethyl-4,4-diethyl*cyclo*hexanol-2	117 to 118° (11 mm.)	0.915	1.4730 (20°)	—
1,1-dimethyl-4,4-diethyl*cyclo*hexanone-2	233 to 235° (742 mm.)	0.907	1.4609 (20°)	—

[1]) *Liebigs Annalen* **230** (1885), 257. — [2]) *Ibidem* **401** (1913), 303. — [3]) *Ibidem* **409** (1915), 149.

Hydrocarbons.

Hydrocarbons from hydroaromatic alcohols and ketones.

K. von Auwers, together with W. Treppmann and F. Krollpfeiffer[1]), investigated some unsaturated hydroaromatic hydrocarbons and ketones. Dehydration of 1-phenyl-*cyclo*hexanol yielded phenyl*cyclo*hexene, $C_{12}H_{14}$, on which Friedmann and Bauer[2]) have reported already. From 1-benzyl*cyclo*hexanol-1 or phenyl*cyclo*hexylcarbinol, 1-benzyl-*cyclo*hexene-1, $C_{13}H_{16}$, forms by dehydration. The nitrosochloride of the benzyl*cyclo*-hexene can be converted into the oxime of the 1-benzyl*cyclo*hexene-5-one-2, from which, on hydrolysis with 30 p. c. sulphuric acid, 1-benzyl*cyclo*hexen-5-one-2, $C_{13}H_{14}O$ resulted. By reduction with hydrogen and colloidal palladium it yields 1-benzyl-*cyclo*hexanone-2, $C_{13}H_{16}O$. The action of magnesium-phenylbromide on 1,3-dimethyl-*cyclo*hexen-3-one-5 leads to 1,3-dimethyl-5-phenyl*cyclo*hexanol-5, which passes into 1,3-dimethyl-5-phenyl*cyclo*hexadiene-3,5, $C_{14}H_{16}$ by dehydration. When boiled with sodium and alcohol, this hydrocarbon yields 1,3-dimethyl-5-phenyl*cyclo*hexene-3, $C_{14}H_{18}$. 1-Methyl-3-oxymethylene*cyclo*hexanone-2, $C_8H_{14}O_2$, results through the action of sodium and amyl formate on methyl*cyclo*hexanone. The reduction with palladium and hydrogen leads to 1,3-dimethyl*cyclo*hexanone-2, $C_{18}H_{14}O$, from which, by treatment with methyl iodide and magnesium, 1,2,3-trimethyl*cyclo*hexene-1, C_9H_{16}, forms, an easily mobile liquid of agreeable, mild odour; b. p. 149.6 to 150° (749 mm.).

Mercuric acetate in the investigation of essential oils.

In order to investigate the terpenic portion of volatile oils, L. Balbiano[3]) recommends to use an aqueous solution of mercuric acetate. This reacts, as it is known, with pinene in the heat, forming dihydroxypinene, whereas with camphene it gives a quantitative yield of an unsoluble compound melting at 187°, from which the camphene can be recovered by heating with zinc and dilute hydrochloric acid[4]). Mercuric acetate does not react with either aromatic hydrocarbons, such as cymene, or bicyclic hydrocarbons ($C_{10}H_{18}$) of the pinane type.

Already as far back as 1903[5]), we pointed out that this reaction may be used to advantage in the investigation of volatile oils. We then succeeded, with the aid of the mercuric acetate compound, in isolating camphene from the fractions of Ceylon citronella oil that boil between 158 and 162°, and to characterize it by transforming it into *iso*borneol.

The *therapeutical use of pinene ozonide* has been discussed on p. 71 of this *Report*.

As to the *content of β-pinene in Spanish oil of turpentine,* see p. 40.

Phellandrene. So far, solid, well defined hydrogen haloids had not been prepared from *β*-phellandrene. L. Francesconi and E. Sernagiotto[6]) have now treated *β*-phellandrene, obtained from bupleurum oil, with alcoholic hydrochloric acid, when, in addition to an oily product, terpinene dihydrochloride resulted (m. p. 51 to 52°).

Azulene. On page 87 of our previous *Report*, we discussed a paper by A. E. Sherndal on this interesting, intensely blue hydrocarbon, to which some essential oils owe their colour. The author has meanwhile continued his investigations and has arrived at

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[1]) *Berl. Berichte* **48** (1915), 1207, 1226. — [2]) *Annal. de Chim.* IX. **1** (1914), 384. — [3]) *Berl. Berichte* **48** (1915), 394. — [4]) Comp. *Reports* April **1903**, 85; April **1904**, 100; October **1906**, 101; April **1911**, 118; April **1915**, 44. — [5]) *Report* April **1903**, 86. — [6]) *Gazz. chim. ital.* **44** (1914), II. 456; *Chem. Zentralbl.* **1915**, I. 892.

noteworthy results as to the constitution and the identification of this body[1]). He found that azulene easily forms a picrate, by means of which it can be identified and purified. Sherndal added a mixture of 1 g. of azulene and 5 cc. of alcohol to a solution of 1 g. of picric acid in 20 cc. of 95 p.c. alcohol. In a few minutes the solution set to a mass of crystals, which dissolved again on heating and from which the picrate deposited on cooling in the form of short shiny black needles. It melts at 118°. In order to ascertain the composition of the picrate it was heated with water containing a measured amount of barium hydroxide. By titration of the excess of barium hydroxide, it was found that the picrate contains 1 molecule of azulene and 1 molecule of picric acid.

With the aid of the picrate, the presence of azulene was proved in camphor oil and oil of cubebs, the latter containing only 0.03 p.c. The azulene had been prepared by shaking the oil of cubebs, dissolved in light petroleum, with sulphuric acid.

To give an idea of the colour intensity of azulene, Sherndal dissolved 0.064 g. of the pure hydrocarbon in 1 litre of benzine and tried to obtain the same intensity of colour with an ammoniacal solution of copper sulphate, when 0.24 g. of copper sulphate was required per litre.

Through the action of sulphuric acid and acetic anhydride, blue coloured products were obtained from West Indian sandalwood oil, guaiac oil and oil of gurjun balsam. The sesquiterpene fraction of eucalyptus oil[2]) yielded a greenish-blue oil, whereas no green or blue fractions could be obtained from cedarwood oil and caryophyllene from clove oil.

Sherndal mixed 10 cc. of oil of gurjun balsam with the same volume of acetic anhydride and allowed 2 cc. of concentrated sulphuric acid to flow in gradually, cooling with ice all the while. A violent reaction took place; the mixture turned purple, which colour soon changed into dark blue, and sulphur dioxide was evolved. Some time afterwards the mixture was distilled with steam, when 4 cc. of a dark blue oil were obtained, from which azulene could be isolated by treatment with benzine and sulphuric acid. The yield was 0.04 p.c. The picrate melted at 122°.

On reduction with colloidal palladium and hydrogen, azulene absorbs 8 atoms of hydrogen and forms a colourless hydrocarbon, $C_{15}H_{26}$, which shows the properties of a tricyclic sesquiterpene and is probably identical with dihydro-α-gurjunene ($d_{20°}$ 0.8935; $n_{D20°}$ 1.490; $\alpha_D \pm 0$). Hydrogenated azulene affords an intense colour reaction with acetic anhydride + sulphuric acid and with bromine in acetic acid.

It is evident from the result of the reduction that azulene is closely allied to the sesquiterpenes. It contains four double links and is tricyclic. The easy formation of the picrate indicates that it contains an aromatic nucleus. Conjugate hydroaromatic double links are absent, for it cannot be reduced with sodium and alcohol. The blue colour may be explained by the peculiar arrangement of the double links in the molecule.

Styrene. Some time ago, H. Stobbe and G. Posnjak[3]) investigated the polymerization of styrene into metastyrene, arriving at the following conclusions on account of the results obtained:—

1. The velocity of the polymerization of freshly distilled styrene increases with the time. It is, therefore, abnormal and must be classified among the group of autocatalytic processes.

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[1]) *Journ. Americ. chem. Soc.* **37** (1915), 1537. — [2]) As 140 kinds of eucalyptus oil are known so far, above general indication is insufficient. — [3]) *Liebigs Annalen* **371** (1910), 259. — *Berl. Berichte* **47** (1914), 2701; *Report* April **1915**, 88.

2. Light considerably accelerates the reaction styrene → metastyrene.
3. Styrene which has previously been exposed to the light polymerizes more quickly in the dark than unexposed styrene, so that there is a photochemical after-effect.

The course of the polymerization was, in these experiments, followed by measuring the viscosity.

Stobbe[1]) felt himself bound to support above conclusions in some other way and therefore controlled the speed of the polymerization by determining the refraction of the light. It had previously been established that the refractive index is noticeably increased already by small quantities of metastyrene, dissolved in the styrene. In his new experiments, Stobbe arrived at the same results as before, when he measured the viscosity. In addition to the photochemical after-effect previously mentioned, a thermic after-effect has been observed. Styrene which has been exposed to the light or heated polymerizes more quickly under otherwise equal conditions than preparations to which this has not been done.

The tendency of polymerization is greater in stored than in freshly distilled samples of styrene.

Alcohols.

Linalool. As extremes of optical rotation, the following values have so far been observed; $-20°\,7'$ for linalool from oil of limes and $+19°\,18'$ for linalool from sweet orange oil, whereas we found from -17 to $+13°$ for the technical product of our own manufacture[2]). For linalool recovered from the urethane, a rotation of $-17°\,41'$ was ascertained in our laboratories[3]). We are, therefore, surprised by a communication from V. Paolini and L. Divizia[4]), according to which linalool in an optically pure state is supposed to show only $[\alpha]_D + 1.70$ and $-1.60°$. They treated the hydrogen phthalate of linalool in alcoholic solution with the calculated amount of strychnine. In order to obtain the hydrogen phthalate, they dissolved linalool in light petroleum and added sodium in excess at a low temperature. The molecular quantity of phthalic anhydride was added to the sodium linaloolate, and the resulting sodium salt in aqueous solution treated with dilute sulphuric acid. The linalyl hydrogen phthalate separated as an oil, which was converted direct into its strychnine salt. This was purified by fractionated crystallization from alcohol and yielded on saponification linalool boiling between 197 and 198° ($d_{15°}$ 0.869 to 0.870). The scission of synthetic linalool into its optical antipodes, was carried out after the same method. The less readily soluble strychnine salt of *l*-linalyl hydrogen phthalate (m.p. 155 to 156°) yielded on saponification *d*-linalool of $[\alpha]_D + 1.70°$, whereas from the mother-liquor *l*-linalool of $[\alpha]_D - 1.60°$ was obtained.

The authors do not give any explanation for the fact that this low specific rotation contradicts former observations.

Unlike linalool, myrcenol affords an easily soluble, not crystalline strychnine salt of myrcenyl hydrogen phthalate.

Menthol. In a voluminous paper, N. Kurssanow[5]) reports on the preparation of menthyl chloride and its conversion into menthene, menthol, dimenthyl, and other bodies allied to menthol.

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[1]) *Liebigs Annalen* **409** (1915), 1. — [2]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. I, p. 353. — [3]) *Report* October **1911**, 140. — [4]) *Rend. della R. Accademia dei Lincei*, Roma (5), **23** (1914), II. 171; *Chem. Zentralbl.* **1915**, I. 606. The authors kindly sent us a reprint. — [5]) *Journ. russ. phys. chem. Ges.* **46** (1914), 815; *Chem. Zentralbl.* **1915**, I. 893.

He further discusses the stereochemical structure of menthol and some of its derivatives and finally mentions the conversion of menthylphenyl ether into menthylphenol. Menthylphenol (phenylurethane, m. p. 141°) is obtained by the action of menthylchloride on phenol in the presence of hydrochloric acid at from 165 to 170°. Menthylphenol, when heated with hydrochloric acid, forms menthylchloride and phenol, so that the reaction is reversible. Hydrogen chloride acts as a catalyst, traces of it being sufficient to carry out the reaction. If the hydrochloric acid formed is removed, the yield of menthylphenol can be increased considerably.

Re esters of menthol, see pages 62 and 63.

Borneol. G. Pellini[1]) prepared silicic esters of borneol. By the action of *l*-borneol on silicon tetrachloride, he obtained a mixture of tetra-*l*-bornyl silicate, $(C_{10}H_{17}O)_4Si$ (m.p. 291 to 292°), tri-*l*-bornyl monochlorosilicic ester, $(C_{10}H_{17}O)_3SiCl$ (m. p. 215 to 218°), di-*l*-bornyl dichlorosilicic ester (b. p. 203 to 205° at 10 mm.) and mono-*l*-bornyl trichlorosilicic ester (b. p. 140 to 142° at 760 mm.). The trichloro ester, when heated with silver oxide in anhydrous ether, yields the normal *l*-bornyl ester of dimetasilicic acid, $(C_{10}H_{17})_2Si_2O_5$, which forms glassy scales which soften at 92° but have no definite melting point.

Santalol. V. Paolini and L. Divizia[2]) prepared pure α- and β-santalols by purifying the strychnine phthalate of santalol through fractionated crystallization. For this purpose, they added to santalol, mixed with light petroleum, some potassium and, after this had dissolved, phthalic anhydride. By shaking with slightly alkaline water they extracted the potassium phthalate of santalol, from which the hydrogen phthalate was liberated with the aid of dilute sulphuric acid and then converted into the strychnine salt. The strychnine salts were purified by crystallization from acetic ester and alcohol, until melting point and optical rotation remained constant, when they were saponified.

In this manner pure α-santalol was obtained (b. p. 159° at 10 mm.; $d_{15°}$ 0.979; $\alpha_D + 1°10'$; $n_{D19°}$ 1.499). The strychnine phthalate of α-santalol melts at 155° and shows $[\alpha]_D - 1°40'$.

The following constants were found for β-santalol: b. p. 168 to 169° (10 mm.); $d_{15°}$ 0.9729; $\alpha_D - 42°0'$; $n_{D19°}$ 1.5092. The strychnine phthalate of β-santalol melts between 134 to 135°; $[\alpha]_D - 30°43'$.

According to older observations α-santalol showed α_D down to $-1.2°$, and β-santalol $\alpha_D - 56°$[3]), which latter value deviates considerably from that found by Paolini and Divizia.

Aldehydes.

W. Borsche[4]), in his second communication on the condensation of γ-ketonic acids with aldehydes, describes the condensation of sodium laevulate with anisaldehyde, piperonal, and cinnamaldehyde. He heated dry sodium laevulate with twice its quantity of acetic anhydride and an equal quantity of anisaldehyde for 12 hours on a water-bath and then triturated the warm mass with water. On cooling, a lump of crystals separated, which was repeatedly washed with cold alcohol, when the con-

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[1]) *Gazz. chim. ital.* **45** (1915), I. 380; *Journ. Soc. chem. Industry* **34** (1915), 685. — [2]) *Rend. della R. Accademia dei Lincei*, Roma (5), **23** (1914), II. 226; *Chem. Zentralbl.* **1915**, I. 606. — [3]) Comp. Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. 1, p. 400. — [4]) *Berl. Berichte* **48** (1915), 842. See also *Ibidem* **47** (1914), 1108.

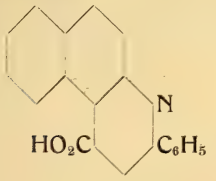
densation-product remained in the shape of dark-yellow needles. In a pure state it melts between 137 and 138°. The compound has the empirical formula $C_{26}H_{26}O_7$. With piperonal (heliotropin), sodium laevulate forms a condensation-product, $C_{26}H_{22}O_9$, melting at 187°, with cinnamaldehyde another of the formula $C_{28}H_{26}O_5$, melting at 166°.

In a paper by J. Kendall and W. A. Gibbons[1]) on the addition compounds of aldehydes and ketones with organic acids, which lies generally speaking in the physico-chemical domain, the following solid derivatives are described; benzaldehyde-trichloroacetic acid, C_7H_6O, CCl_3CO_2H (m. p. 8,4°), anisaldehyde-trichloroacetic acid, $C_8H_8O_2$, CCl_3CO_2H (m. p. 30,9°), vanillin-trichloroacetic acid, $C_8H_8O_3$, $2CCl_3CO_2H$ (m. p. 14,3°) and piperonal (heliotropin)-trichloroacetic acid $C_8H_6O_3$, $2CCl_3CO_2H$ (m. p. 37,4°), $C_8H_6O_3$, CCl_3CO_2H (m. p. 35°).

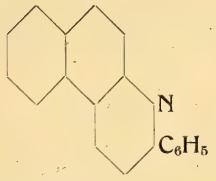
Citronellal. Following up the investigations of Ciamician and Silber, repeatedly discussed in our *Reports*, regarding the exposure of terpenes to the light, E. Sernagiotto[2]) examined citronellal as to its behaviour in direct sunlight and in the presence of oxygen. It yielded under these circumstances acetic acid, β-methylhexoic acid, menthone (semicarbazone, m. p. 184 to 185°), a ketone apparently unknown so far, $C_{10}H_{18}O$ (semicarbazone, m. p. 206 to 207°), *iso*pulegol (identified by its oxidization to *iso*pulegone), acetone, β-methyladipic acid (m. p. 84°), and dihydroxycitronellic acid, an oil which cannot be crystallized. As may be seen, citronellal, on autoxidation in the light, yields on the one hand isomerization products, which also result by the action of acids or acetic anhydride, such as *iso*pulegol, and oxidation products of the bodies formed through isomerization, such as menthone, which is likewise obtained on oxidizing with chromic acid. On the other hand, true oxidation products result, e. g. dihydroxycitronellic acid, obtainable also by oxidation with potassium permanganate, and β-methyladipic acid, which also results by oxidation with chromic acid mixture.

As to the composition of commercial citronellal, see page 74 of this *Report*.

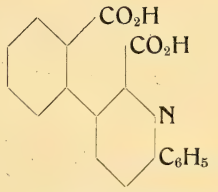
Benzaldehyde. When O. Doebner described at the time his well known reaction[3]), he ascribed the structure expressed by formula I to the phenylnaphthacinchonic acid, which forms for instance by the action of benzaldehyde and β-naphthylamine on



(I) Phenylnaphthacinchonic acid.



(II) α-Phenyl-β-naphthaquinoline.



(III) Diphenylpyridinedicarboxylic acid.

peruvic acid. The proof of the correctness of this opinion has now been given by R. Ciusa and G. Buogo[4]), who oxidized the α-phenyl-β-naphthaquinoline (II), formed from cinchonic acid, with potassium permanganate dissolved in acetone to diphenylpyridinedicarboxylic acid (III).

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[1]) *Journ. Americ. Chem. Soc.* **37** (1915), 149. — [2]) *Atti R. Accad. dei Lincei*, Roma (5) **24** (1915), 850; *Chem. Zentralbl.* **1915**, II. 468. — [3]) *Berl. Berichte* **27** (1894), 352; *Report* April **1894**, 27. — [4]) *Atti R. Accad. dei Lincei*, Roma (5), **23**, II. (1914), 262, 265; *Chem. Zentralbl.* **1915**, I. 746, 747.

In a paper by G. Reddelien[1]) on the addition products of nitric and picric acids with unsaturated organic compounds we find the description of the picrates of benzaldehyde and cinnamaldehyde. The picrate of benzaldehyde forms when picric acid is dissolved in benzaldehyde under heating; it crystallizes in splendid light-yellow prisms of about 1 cm. in length, melting at from 70 to 72°. It is fairly unstable, the crystals decay quickly, losing benzaldehyde. In order to prepare the picrate, cinnamaldehyde is saturated with picric acid at about 70° and then cooled in a freezing mixture. It forms light-yellow prisms melting at 66 to 67°, which after some time take the smell of cinnamaldehyde but are very stable, generally speaking.

As to the formation of benzaldehyde by means of tyrosinase, see p. 68.

Cinnamaldehyde. In order to reduce cinnamaldehyde, E. Róna[2]) added yeast to a sugar solution and, after the fermentation had started, cinnamaldehyde, when cinnamalcohol resulted.

o-*Vanillin.* Whilst the derivatives of vanillin and piperonal (heliotropin) are well investigated, little is known regarding those of *o*-vanillin and *o*-veratraldehyde, as they are accessible only with difficulty. In order to fill this gap at least in part, W. H. Perkin and R. Robinson[3]) prepared some derivatives of these aldehydes, viz., those of benzoic acid, benzyl alcohol, cinnamic acid, phenylpropionic acid, hydrindone, and other simple derivatives of the *o*-veratric series.

Homovanillin. As stated on p. 103 of our previous *Report,* C. Harries and R. Haarmann obtained on reduction of normal eugenolozonide homovanillin as a thick oil, which, as per the results of the analysis, was not perfectly pure. When distilled under reduced pressure (0,25 mm.), as Harries[4]) says in a later publication, homovanillin boiled between 105 and 106° and congealed on standing at a low temperature to a white crystalline mass, from which homovanillin in a chemically pure state could be obtained by treatment with carbon disulphide and carbon tetrachloride. It melts at from 50 to 50.5° and smells agreeably, flower-like, somewhat less strongly than vanillin but perhaps more like vanilla. The *p*-nitrophenylhydrazone melts at 154.5°. Homovanillin is a very sensitive body which, on distillation *in vacuo,* leaves a syrupy, red residue.

Ketones.

Anhydroxylamines of unsaturated ketones.

As Semmler[5]) found at the time, an anhydro-compound, the imino-base $C_{10}H_{17}NO$, results from pulegonehydroxylamine by splitting off water. Harries obtained in a similar way an anhydro-compound from diacetonehydroxylamine; santolinenone[6]), the structure of which is analogous with that of pulegone, likewise yields an imino-base in this way. L. Francesconi and G. Sanna[7]) conjecture therefore that anhydro-bases generally result from the hydroxylamino compounds of cyclic $\alpha\beta$-unsaturated ketones, the double-linking

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[1]) *Journ. f. prakt. Chem.* II. **91** (1915), 239. — [2]) *Biochem. Zeitschr.* **67** (1914), 137; *Chem. Zentralbl.* **1915**, I. 619; comp. *Report* April **1915**, 91. — [3]) *Journ. Chem. Soc.* **105** (1914), 2376. — [4]) *Berl. Berichte* **48** (1915), 868. — [5]) *Berl. Berichte* **37** (1904), 305, 134; *Report* October **1904**, 124. — [6]) Comp. *Report* April **1915**, 41. — [7]) *Gazz. chim. ital.* **45** (1915), I. 35; *Chem. Zentralbl.* **1915**, I. 1117.

of which is outside the nucleus, as well as from some aliphatic $\alpha\beta$-unsaturated ketones. They obtained anhydropulegonehydroxylamine by treating pulegonehydroxylamine with an ethereal solution of hydrogen chloride gas. If the hydrochloric acid is allowed to act longer, the normal pulegoneoxime seems to form. Camphorone, when boiled with hydroxylamine hydrochloride and sodium bicarbonate in alcoholic etheral solution, passes into camphoronehydroxylamine, melting at 120°. With hydrochloric acid in ethereal solution it forms anhydrocamphoronehydroxylamine, an oil that smells like coniine. It seems to convert itself into camphoroneoxime (m. p. 115°) when kept in contact with water. The oxalate melts at 170°.

Methylheptenone. In his 118th treatise on terpenes and essential oils, O. Wallach[1]) reports on the derivatives of methylheptenone and allied compounds. Three isomerides of methylheptenone are possible, owing to the different position of the double linking. They may be distinguished as $\alpha\beta$- and γ-methylheptenone (the better known). There is, besides, a δ-isomeride, unknown so far.

α $(CH_3)_2CHCH_2CH:CHCOCH_3$ $\quad$ γ $(CH_3)_2C:CHCH_2CH_2COCH_3$

β $(CH_3)_2CHCH:CHCH_2COCH_3$ $\quad$ δ $CH_3C:(CH_2)CH_2CH_2CH_2COCH_3$

All the four modifications, on addition of hydrogen to the ethylene linking, ought to yield the same saturated methylheptanone (a methylhexylketone), which Wallach prepared some time ago by reducing β-methylheptenone with palladium and hydrogen[2]). It was made evident by experiments that the ethylene linking in $\alpha\beta$-position absorbs hydrogen more readily than that in $\gamma\delta$-position. α-Methylheptenone in alcoholic solution can be reduced with sodium to the saturated methylheptanol, whereas γ-methylheptenone yields under the same conditions methylheptenol as final product.

The so-called *iso*methylheptenone, an *iso*propylbutenyl ketone, is isomeric with the methylheptenone just mentioned. The derivatives of *iso*methylheptenone smell quite different from the analogous ones of γ-methylheptenone. Whilst the odour of these is pleasant, that of the others is sharp and rather disagreeable. The position of the oxygen in the molecule is thus very noticeable.

By treatment with magnesium ethyl iodide, methylheptanone yields tetrahydrolinalool, an alcohol which Barbier also prepared a short while ago[3]). By splitting off water with the aid of zinc chloride, tetrahydrolinalool afforded a hydrocarbon, $(CH_3)_2CHCH_2CH_2CH_2C(CH_3):CHCH_3$, which on oxidation with potassium permanganate passed into methylheptanone (semicarbazone, m. p. 156°). The same hydrocarbon is obtained by treatment of methylheptanone with zinc and ethyl bromopropionate. The experiments with a view to prepare from the nitrosate of the hydrocarbon an unsaturated ketone with 10 carbon atoms had not the desired success.

The action of hypobromite on methylheptanone leads to heptoic acid. Through the action of several molecules of bromine on methylheptanone, and consecutive treatment with alcoholic alkali, an acid is formed that contains 8 carbon molecules. Sufficient explanation for this behaviour was found in the course of the investigation.

The *iso*propyl-*n*-butylketone, obtained on reducing *iso*propylbutenyl ketone (*iso*methylheptenone) according to Paal or Skita, boiled between 158 and 159°. The reduction of the ketone in moist ethereal solution leads to *iso*propyl-*n*-butylcarbinol (b. p. 167 to 168°), in addition to a pinakone. The interaction of *iso*propylbutenyl ketone and *iso*propylbutyl ketone with Grignard's reagent does not take place so smoothly

[1]) *Liebigs Annalen* **408** (1915), 183. — [2]) Comp. *Report* April **1911**, 165. — [3]) Comp. *Report* April **1915**, 90.

as is the case with γ-methylheptenone. The following derivatives were prepared: methyl*iso*propylbutenylcarbinol (b. p. 174 to 177°), ethyl*iso*propylbutenylcarbinol (b. p. 188 to 191°), and ethyl*iso*propylbutylcarbinol (b. p. 191 to 195°). As pointed out before, these compounds have an unpleasent smell.

*Trimethyl*cyclo*pentenone.* When splitting methyl amylenenitrolacetoacetate with alkali, Wallach, some years ago, obtained an unsaturated ketone, $C_8H_{12}O$, which had to be considered as trimethyl*cyclo*pentenone[1]). Wallach[2]) recently repeated this reaction. The trimethyl*cyclo*pentenone, $C_8H_{12}O$, forms a ketone of peppermint-like odour and the semicarbazone of which (according to the way of heating) melts at 200 or 210°. It was reduced after Skita's method, when it yielded trimethyl*cyclo*pentanone, $C_8H_{14}O$, boiling between 164 and 167°; $d_{19°}$ 0.8829; n_D 1.4336; semicarbazone, m. p. 209°; oxime, m. p. 105°.

If treated with sodium ethoxide, instead of aqueous potassa, methyl amylenenitrolacetoacetate shows an entirely different behaviour. It passes over into a yellowish-brown body, $C_{10}H_{13}NO_5$, which is stable in contact with air and almost insoluble in organic liquids.

Iso*propyl*cyclo*hexanone.* A. W. Crossley and W. R. Pratt[3]) report on the preparation of *iso*propyl*cyclo*hexan-3-one, which might serve as raw material for such terpenes as are derived from *m*-cymene. They treated *iso*propyldihydroresorcin with phosphorus trichloride, when 5-chloro-1-*iso*propyl-Δ^4-*cyclo*hexen-3-one resulted, the constitution of which was proved by its oxidation to β-*iso*propylglutaric acid. The chloro*iso*propyl-*cyclo*hexenone can, with the aid of sodium, be reduced in moist ethereal solution to 1-*iso*propyl*cyclo*hexan-3-ol, of which a *trans*- and a *cis*-isomeride seem to exist. On oxidation with potassium dichromate and sulphuric acid, the alcohol passes into the ketone 1-*iso*propyl*cyclo*hexan-3-one, a colourless liquid of pungent camphoraceous odour: b. p. 119° (62 mm.), 208° at ordinary pressure. The semicarbazone melts at 186 to 187°, the oxime boils at 155° (37 mm.), and the benzoyl derivative melts at 91 to 92°. *Iso*propyl*cyclo*hexanone is but slowly attacked by potassium permanganate, when acetic and β-*iso*propyladipic acids are formed.

α- *and* β-*Thujamenthone.* On reduction of *iso*thujone according to Paal or Skita, a saturated body, thujamenthone, is obtained[4]). A closer investigation of this ketone lead Wallach[5]) to the unexpected result that it is not identical with the thujamenthone which had previously been prepared in another way. The two compounds differ considerably in their behaviour, on account of which Wallach named them α- and β-thujamenthone.

The long-known α-thujamenthone is obtained by reducing *iso*thujone in alcoholic solution with sodium to thujamenthol, which is then oxidized with chromic acid[6]). In order to obtain a reliably pure body, Wallach first oximated the ketone and repeatedly recrystallized the oxime. The ketone, regenerated from the oxime (m. p. 97°), was treated with semicarbazide; the semicarbazone melted at 185°. The ketone recovered from the semicarbazone boiled at 209 to 209,5° ($d_{18°}$ 0.8915; n_D 1.4474). α-Thujamenthol,

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[1]) J. Rechenberg, *Inauguraldissertation*, Göttingen 1902, p. 30. — [2]) *Liebigs Annalen* **408** (1915), 202. — [3]) *Journ. chem. Soc.* **107** (1915), 171. — [4]) Comp. *Report* April **1911**, 165. — [5]) *Liebigs Annalen* **408** (1915), 163. — [6]) Comp. *Report* October **1902**, 99.

obtained by reduction of α-thujamenthone in alcoholic solution with sodium, boiled at from 212 to 214°; $d_{19°}$ 0.8990; n_D 1.4611. On oxidation with chromic acid, it regenerated the ketone; when heated with zinc chloride, it formed thujamenthene boiling between 163 and 165°. The reduction of the oxime of α-thujamenthone in alcoholic solution with sodium led to α-thujamenthylamine (b. p. 196 to 197°), which on treatment with nitrous acid yielded, in a normal way, α-thujamenthol in addition to the hydrocarbon.

In order to arrive at the β-thujamenthone, two ways may be chosen: either *iso*-thujone is reduced direct according to Skita with palladium chloride ($PdCl_2$) and hydrogen, or one starts from the pure oxime of *iso*thujone, melting at 119 to 120°, reducing it in the presence of palladium and hydrogen. Thus is obtained, in scanty yield, it is true, the oxime of β-thujamenthone, which is decomposed on being heated with acids. It melts between 130 and 131°, the semicarbazone between 190 and 191°. The β-thujamenthone regenerated from the latter melts at from 215 to 216.5°; $d_{19°}$ 0.8990; n_D 1.4511. On heating with sulphuric and glacial acetic acids, the oxime of β-thujamenthone is converted into an *iso*oxime melting at 102°. β-Thujamenthol (obtained by reducing β-thujamenthone with sodium and alcohol) boiled at from 216.5 to 217.5°; $d_{19°}$ 0.8995; n_D 1.4583. It yielded again β-thujamenthone on oxidation with chromic acid. When heated with zinc chloride, β-thujamenthol passed into thujamenthene. By reduction with sodium and alcohol, the oxime of β-thujamenthone was converted into β-thujamenthylamine (b. p. 206.5°), the hydrochloride of which was subjected to the action of sodium nitrite, when a probably tertiary thujamenthol was formed (b. p. 204°). Dehydration of this thujamenthol led to another hydrocarbon than the dehydration of the two thujamenthols just described. Whereas the thujamenthenes from α- and β-thujamenthol do not form any solid nitrosochlorides, thujamenthene from tertiary thujamenthol affords a sparingly soluble, labile nitrosochloride melting at 108°. By splitting off hydrochloric acid it forms the oxime of *iso*thujone. The sequence of reactions indicated proves that β-thujamenthone may be reconverted into *iso*thujone, from which it was prepared.

Wallach considers α- and β-thujamenthone as physically isomeric, but it has not been possible to establish anything which would point to the presence of chemical isomerism. The fact that the physical isomerides described show different boiling points is striking.

As to the *scission of santolinenone into the optical antipodes* see p. 35 of this *Report*.

Phenols and phenol ethers.

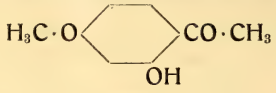
The action of nitrosobenzene on phenol ethers.

On p. 150 of our *Report* October **1911**, we discussed a paper by Angeli, Alessandri, and Pegna on the action of nitrosobenzene on unsaturated compounds. The study has meanwhile been continued by L. Alessandri[1]). He examined the action of nitrosobenzene on estragole, myristicin and methyleugenol, when three yellow compounds resulted, melting at 165°, 180° and 154°, respectively. Their constitution is probably analogous to that of the compound previously obtained from safrole. The action of nitrosobenzene on apiole goes on in a somewhat different manner; a yellow substance results (m. p. 137°) which probably represents the aldehyde $(CH_3O)_2(CH_2O_2)C_6H \cdot CH : CH \cdot CHO$

[1]) *Atti R. Accad. dei Lincei*, Roma (5), **24** (1915), 62; *Chem. Zentralbl.* **1915**, II. 1210.

and may be called apiole acraldehyde. In addition to the yellow compound, a colourless one forms, probably apiolaldehyde, which melts at about 100°. From asarone and nitrosobenzene, the N-phenylether of asarylaldoxime, $(CH_3O)_3C_6H_2 \cdot CH : N(C_6H_5) : O$, is obtained; it melts at 125°. Besides, asarylaldehyde and azoxybenzene result. It was impossible to isolate any well-defined reaction product when nitrosobenzene was allowed to act on *iso*safrole.

Paeonol. Many years ago already, Tahara[1]) synthetically prepared, by methylating resacetophenone, the phenol paeonol, i. e. the *p*-methylether of resacetophenone (*p*-methoxy-*o*-hydroxyphenylmethylketone), which occurs in the oil of *Paeonia Moutan*, Sims., (N. O. *Ranunculaceae*). Another synthesis of paeonol has been described by K. Hoesch[2]), who poured 30 cc. of ether over 5 g. resorcinol monomethylether, 3 g. acetonitrile and 2 g. zinc chloride, and then let hydrogen chloride pass through the solution for 4 or 5 hours. After some time, a crystalline deposit formed, which



Paeonol.

process was completed in 4 or 5 hours. The wine-red deposit discoloured at once if water was poured over it. After having shaken it with ether, he distilled the aqueous solution with steam, when the volatile paeonol passed over, whereas the non-volatile isomeric *iso*paeonol remained in the flask.

Acids.

Caronic acid. As it is known, two dibasic acids form on oxidation of carone a *cis*- and a *trans*-caronic acid (*gem.*-dimethyl*cyclo*propane dicarboxylic acid)[3]). R. Locquin[4]) now reports on some derivatives of these acids. He describes the dimethylester of the *cis*-caronic acid as a colourless, readily mobile liquid boiling at from 111 to 112° (14 mm.); the diethylester, he says, reminds one by its smell of diethyl succinate.

Nopinic acid. On a former occasion, E. Dorronsoro and E. Fernández believed to have observed an intense colouration of nopinic acid with resorcinol and sulphuric acid. As they[5]) ascertained later on, this colour reaction is not caused by nopinic but by the oxalic acid, which abundantly forms on oxidation of turpentine oil with potassium permanganate.

Oxides.

The conversion of cineol into peroxides of unknown composition has been mentioned on page 72 of this *Report*.

Re quantitative estimation of cineol, compare page 17.

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[1]) *Berl. Berichte* **24** (1891), 2459. — [2]) *Ibidem* **48** (1915), 1122. — [3]) A. v. Baeyer and W. Ipatiew, *Berl. Berichte* **29** (1896), 2796. — See also *Report* April **1910**, 176. — [4]) *Bull. Soc. chim.* IV. **15** (1914), 747. — [5]) *An. Soc. Esp. Ph. Ch.* **11** (1913), 441; *Bull. Soc. Chim.* IV. **16** (1914), 300.

Nitrogenous bodies.

Together with G. F. Morrell, Harries[1]) reports on some reactions of dihydrocarvylamine, dihydroterpinylamine and carvylamine. As Morrell[2]) had found before, the oxidation of benzoyldihydrocarvylamine with ozone leads to 1-methyl-2-benzoylamino-4-acetyl*cyclo*hexane, the ketone properties of which were established by converting it into a semicarbazone (m. p. 200°) and a nitrophenylhydrazone (m. p. 252°). By ozonization of β-benzoyldihydroterpinylamine, *trans*-2-benzoylamino-1-methyl*cyclo*hexanone-4 (m. p. 150 to 151°) was obtained, whereas the formerly described *cis*-2-benzoylamino-1-methyl*cyclo*hexanone-4 results from the α-benzoyl derivative. The semicarbazone of this ketone melts at 194°, the nitrophenylhydrazone at 248°.

The authors further report on the conversion of dihydroterpinylamine into a menthadiene by dry distillation of dihydroterpinylamine phosphate. Terpinene formed in addition to the menthadiene.

The little investigated carvylamine, which Goldschmidt and Kisser as well as Goldschmidt and Fischer[3]) obtained in a poor yield by reducing carvonoxime with zinc dust and acetic acid, has now been prepared with a much better yield by Harries and Morrell, who reduced carvonoxime in glacial acetic acid and alcohol with zinc dust under cooling with ice. The base is a colourless liquid of feeble odour and boiling at from 94 to 95° (12.5 mm.). The hydrochloride melts at about 220°, the α-benzoyl derivative at 174°. The β-benzoyl derivative (m. p. 110°) had formed in only a very small quantity. Like dihydrocarvylamine, carvylamine combines with two molecules of hydrogen chloride, thus forming the hydrochloride of a chlorinated base. The dihydrochloride melts at about 145°. By splitting off hydrogen chloride from the chlorinated base on heating with pyridine, terpinylamine forms, possibly in two isomerides, and a considerable quantity of regenerated carvylamine likewise results.

Finally, Harries and S. Smith report on some derivatives of dihydrocarvylamine. When this base is boiled with acetic anhydride, acetyldihydrocarvylamine (m. p. 131 to 132°) results, which Wallach had prepared already. Oxidation of this base with ozone leads to 1-methyl-2-acetylamino-4-ethanoyl*cyclo*hexane melting at 193 to 194°. The action of anhydrous formic acid on dihydrocarvylamine leads to a body melting between 152 and 153°, perhaps formyldihydroterpinylamine. By the action of ethyl formate on dihydrocarvylamine, formyldihydrocarvylamine results (b. p. 179 to 189° at 15 mm.), which on oxidation with ozone yields 1-methyl-2-formylamino-4-ethanoyl *cyclo*hexane (m. p. 120 to 121°). The following oxalic acid derivatives of dihydrocarvylamine are worth mentioning: oxalyldihydrocarvylamine, melting at 250°, and semioxalyldihydrocarvylamine (m. p. 94°). Both compounds form on heating dihydrocarvylamine with oxalic acid. The semioxalyldihydrocarvylamine was converted into the semioxalyl compound of the 1-methyl-2-amino-4-ethanoyl*cyclo*hexane (m. p. 107°) by oxidizing it with ozone in glacial acetic acid. Carbethoxydihydrocarvylamine was prepared according to Claisen's method by heating the ethereal solution of the amine with ethyl chlorocarbonate in the presence of dried potassium carbonate. It melts at 88°. It was converted into 1-methyl-2-carbethoxamino-4-ethanoyl*cyclo*hexane by ozonization in acetic acid. On heating the carbethoxyamino ketone with hydrochloric acid in a sealed tube, the hydrochloride of 1-methyl-2-amino-4-ethanoyl*cyclo*hexane (m. p. 183 to 185°) is formed. The free base melts between 119 and 122°; b. p. 65 to 68° at 11 mm.

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[1]) *Liebigs Annalen* **410** (1915), 70. — [2]) *Berl. Berichte* **44** (1911), 2560; *Report* April **1912**, 197. — [3]) *Berl. Berichte* **20** (1887), 486; **30** (1897), 2069.

Allyl mustard oil. According to G. Rossi[1]), the action of *o*-toluidine on allyl mustard oil at boiling temperature does not lead to allyltolylthiourea as per Hofmann's reaction, but to ditolylthiourea, $C_{15}H_{16}N_2S$, melting at 158°. If *o*-aminobenzoic acid is used instead of *o*-toluidine, a molecular transposition takes place together with an oxidation, when the *o*-aminobenzoic acid is converted into *o*-nitrophthalic acid, which yields the corresponding dianilide with the aniline that forms. The allyl mustard oil is at the same time converted into allyl cyanide, C_3H_5CN.

[1]) *Gazz. Chim. ital.* **44** (1914), II. 264; *Chem. Zentralbl.* **1915**, I. 667.

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on

Essential Oils,

Synthetic Perfumes, &c.

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Contents.

	Page
Scientific and other notes on essential oils	5
Chemical preparations and drugs	64
Notes on scientific research work in the domain of terpenes and essential oils.	
General	81
Bibliography	86
Analytical	88
Physical	96
Botanical	99
Phyto-physiological	100
Physiological	103
Pharmacological	107
Chemical	107
Hydrocarbons	113
Alcohols	117
Aldehydes	120
Ketones	122
Phenols and Phenol ethers	130
Acids and Lactones	132
Nitrogenous bodies	135

List of abbreviations.

d = specific gravity.
$d_{20°}$ = specific gravity at 20° (in references from our laboratories uniformly compared with water at 15°).
$d_{4°}^{20°}$ = specific gravity at 20°, compared with water at 4°.
$\alpha_{D20°}$ = optical rotation at 20°, in a 100 mm. tube.
$[\alpha]_D$ = specific rotation.
$n_{D20°}$ = index of refraction at 20°.
sol. p. = solidifying point.
m. p. = melting point.
b. p. = boiling point.
n = normal.
acet. = acetylation.
acid v. = acid value; ester v. = ester value; sap. v. = saponification value.
g. = gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.
The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

Scientific and other Notes on Essential Oils.

Oil of Anise. The favourable results obtained with essential oils in the treatment of lice-infested clothes have led to experiments being carried out as regards the treatment of itch. It was found that for this complaint the best remedy was anise oil. A. Parutz[1]) recommends application of the oil in the form of an ointment (*ol. anisi* 1.0, vaseline *ad* 100.0). Patients should rub the ointment all over the body, more especially into the places exposed to itch such as the inner side of the joints, between the fingers, in the armpits, around the sacrum, &c. Even after the first inunction the itching sensation is said to cease, after four inunctions the subjective symptoms disappear and the cure is complete. It is, however, advisable that a fifth application of the ointment should be made. A warm bath the day after every treatment is indicated.

Oil of Sweet Basil. V. Lubimenko and M. Novikoff[2]) have attempted to ascertain in how far the formation of essential oil in the plant is influenced by different intensities of light. For this purpose they carried out a few shading experiments on sweet basil *(Ocimum basilicum,* L., N.O. *Labiatæ).* The experimental field had a southern exposure and consisted of four equal parts, one of which remained uncovered while the others had horizontal cloth shades stretched above them at a height of one meter from the soil. The texture of the cloth varied with each plot and was such that the threads only represented 10, 25 and 50 per cent. of the surface respectively. When the plants were in full bloom they were distilled in a current of steam, when it was found that the percentage of water in the plants was increased by increased shading and that the stems also were longer. The greatest growth was observed with 10 per cent. shading; where the shading was 50 per cent. the development of the plant was seriously affected. The production of essential oil appeared to be best in the field subjected to 10 per cent. shading.

Oil of Bay. H. A. Tempany and W. Robson[3]) consider it desirable that a central place for the distillation of bay oil should be erected in the West Indies, so as to render it possible to secure uniformity in quality. To this end the central distillery should be under competent control.

As regards the possibility of increasing consumption of bay oil, the English contemporary, from which we cull these notes, seems to be rather optimistic. Nothing definite is known about the total output of the West Indies. The United States import about 2000 lbs. annually and in Great Britain about 4000 to 5000 lbs. are handled every year, part of which appears to be re-exported from the United States. It is hoped that with regular supplies of even quality, and at a somewhat lower price new markets could be found for bay oil which, so far, was used almost exclusively for the production of bay rum.

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[1]) *Wiener klin. Wochenschr.* **1915**, No. 37; *Vierteljahrsschr. f. prakt. Pharm.* **12** (1915), 352. — [2]) From a reference in the *Americ. Perfumer* **10** (1915), 265. It does not appear from the paper in question where the original treatise was published. — [3]) *Journ. Imp. Agric. Dept. for the West Indies; Perfum. Record* **7** (1916), 209.

On page 25 of our *Report* October **1912** we published a paragraph on experiments in the cultivation of the bay tree in Montserrat. Robson[1]) now reports on the results of the further experiments carried out since then. It appears that the experimental plot is in a vigorous condition and that the yield of oil has become better every year, but that the phenol content declined, amounting in 1912 to 55.5 per cent. (density of the oil 0.9484), in 1913 to 56.2 per cent. (d 0.9460), and in 1914 to 50.5 per cent. (d 0.9342). The cause of this decline is not to be looked for in conditions of cultivation, but is due to the shortness of distillation (6 hours), for on continuing distillation, heavier oils were obtained which contained more phenol. Thus in the Government laboratory at Antigua 150 lbs. of fresh leaves were distilled for nine hours, each hours' distillate being collected, measured, and examined, when the following results were found: —

	Oil obtained in cc.	Phenol content.	Specific gravity
1st. hour	519 cc.	23 per cent.	0.8669
2nd. „	126 „	78 „ „	0.9241
3rd. „	98 „	89 „ „	1.0259
4th. „	96 „	93 „ „	1.0381
5th. „	69 „	95 „ „	1.0409
6th. „	58 „	96 „ „	1.0432
7th. „	53 „	99 „ „	1.0434
9th. „	38 „	96 „ „	1.0436

An oil obtained by nine hours' distillation showed a specific gravity of 0.9742 and contained 60 per cent. of phenols.

In order to ascertain whether bay oil deteriorates in quality on keeping Tempany examined an oil which had been kept for two and a half years.

He found only a slight rise in density, due, probably, to the polymerisation of the hydrocarbon myrcene. There was no change, however, in the phenol content.

Oil of Boswellia serrata. *Boswellia*[2]) *serrata*, Roxb. (N. O. *Burseraceæ*) is a moderate-sized gregarious Indian tree; in North-West India there occurs a variety called *B. serrata* var. *glabra*[3]). A gum-resin exudes from the tree on injury (Boswellia turpentine). In the Punjab this is collected twice a year, in March from incisions made in the previous October, and in June from incisions made in March. Each tree is said to yield annually about 2 lbs. of gum-resin which is employed by the natives in the treatment of rheumatism and nervous diseases, and is also an ingredient in certain ointments. In Gujerat it is burnt as incense in religious ceremonies. The export of Boswellia resin is but small, amounting to 778 cwts., of value £ 1339 in 1913/14, most of which was shipped to Germany and Austria-Hungary.

In the Forest Research Institute in Dehra Dun experiments have been conducted with a view to ascertaining the best method of treating the crude gum-resin in order to obtain turpentine oil, rosin, and other products. The gum and impurities were separated from the resin and oil by treating a quantity of the raw product in a false-bottomed copper still and passing steam through by means of a compound steam coil fitted with spur pipes. By this means small quantities of the most volatile constituents were distilled off, but the resin and most of the oil passed through the false

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[1]) *West Indian Agricultural News* of January 15th., 1916; *Perfum. Record* **7** (1916), 34. — [2]) We would like to remind our readers that oil of olibanum also originates from a species of *Boswellia*, i. e. from *Boswellia Carterii*, Birdw. See Gildemeister und Hoffmann, *Die ätherischen Öle*, 2nd. ed., vol. III, p. 123. — [3]) *Bull. Imp. Inst.* **13** (1915), 351.

bottom, leaving the gum and impurities above. The oil was then separated from the resin by steam distillation and the resultant oil fractionally distilled up to 155°. The turpentine oil obtained in this manner consisted almost wholly of dextro-pinene and contained also limonene or dipentene.

The Boswellia turpentine oil was examined at the Imperial Institute in London; it was found to have the following constants: $d_{15°}$ 0.8446, α_D + 31° 24′, ester v. 2.6, ester v. after acet. 36.4. 89 per cent. of the oil boiled from 153 to 160° and 11 per cent. from 160 to 180°; it possesses satisfactory siccative properties and will, presumably, be found useful for industrial purposes.

Oil of Bupleurum fruticosum. L. Francesconi and E. Sernagiotto[1]) have observed that the oil of this umbellifera, whose content of β-phellandrene had been recognized by them at an earlier date[2]), shows in its various fractions a yield of nitrosochloride of almost constant optical rotation, which yield is the greater, the lower the optical rotation of the respective fraction, and moreover, that the α-phellandrene, under the same conditions as β-phellandrene, yields no nitrosochloride. From this it might be concluded that the active β-phellandrene possesses a specific rotation approximately corresponding with the indications of Pesci, Wallach, and Schimmel & Co. (*viz.*, between + 14.45 and 18.54°) and that in the fractions possessing a higher optical rotation (up to + 65.02°), another isomeride, probably the α-isomeride, is present in corresponding quantities. The fact, however, that not only the yield of nitrosite but also its optical rotation is constant in the various fractions of the oil, leads to the supposition that β-phellandrene possesses a specific rotation of + 65.2° and that the fractions exhibiting lower activity are mixtures of the two optical antipodes with the dextrorotatory form always preponderating. The result of the oxidation with permanganate of potash is in agreement with this, tetrahydrocuminaldehyde being obtained, but no α-hydroxy-β-*iso*-propylglutaric acid, the oxidation product of α-phellandrene. This is also in agreement with the behaviour in the formation of the nitrosochloride, as an analogous case occurs with α-pinene whose yield of nitrosochloride is the greater, the lower the optical rotation of pinene.

β-Phellandrene of the oil from *Bupleurum fruticosum* is identical with the one from *Phellandrium aquaticum*. In alcoholic solution and in the presence of alcoholic hydrochloric acid (but not in glacial acetic acid) it produces a nitrosochloride the yield of which is the greater, the lower the optical rotation of phellandrene. α_D average — 206°. By crystallization it may be split up in two isomerides, α-nitrosochloride, (α_D — 175°; m. p. 101 to 102°) and β-nitrosochloride (α_D — 285°; m. p. 100°). On decomposition with glacial acetic acid the nitrosochloride yields $\Delta^{2,5}$-dihydrocuminaldehyde and carvacrol, as well as cuminaldehyde by secondary oxidation effect of the hydroxylamine. It follows that the crystallized nitrosochloride of β-phellandrene is a mixture of two structural isomerides. The nitrosobromide of β-phellandrene is a white crystalline unstable body. The nitrosite of β-phellandrene melts at 97 to 98°; $[\alpha]_D$ 159.19° (in chloroform); α-phellandrene yields no crystalline nitrosochloride.

Oil of Bystropogon mollis. According to A. Dœring[3]) Argentine mint (*Bystropogon mollis*, Kth., N. O. *Labiatæ*) yields 0.4 per cent. of essential oil; it is a limpid

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[1]) *Gazz. chim. ital.* **46** (1916), I. 119; *Chem. Zentralbl.* **1916**, I. 973. — [2]) Gildemeister und Hoffmann, *Die ätherischen Öle*, 2nd. ed., vol. III, p. 333. — [3]) *Bol. Acad. Nac. Ciencias, Cordoba* **19** (1913), 379; *Journ. Chem. Soc.* **106** (1914), I. 1172.

liquid from which, at a temperature of + 12°, no menthol is separated. d 0.918 to 0.920. The bulk boils at 210°. The oil appears to contain about 2.5 per cent. of furfurol which may be eliminated by treatment with permanganate. It also contains 0.7 per cent. of free acids and traces of phenols, but no menthol. Terpenes could not be characterized so far.

Oil of Cajuput. The following figures are culled from a publication of the Netherlands-Indian San Francisco Committee[1]):

The total exports from the Dutch East Indies amounted to 168233 lbs. in 1912, of which

28218	lbs.	went	to	Holland
2739	„	„	„	Germany
8578	„	„	„	United States
116366	„	„	„	Singapore and
12332	„	„	„	other countries.
Total: 168233	lbs.			

Oil of Calamus. As a note of warning we may here mention a sample of calamus oil submitted to us for analysis by a Leipzig firm. It sailed under the proud designation of *Oleum Calami*, Ph. G. V. but was found to be a concoction containing *i. a.* a safroly camphor oil fraction as well as traces of salicylic acid and apparently also benzoic acid. Its suspiciously weak odour showed that there was but little calamus oil in the mixture. Of the chemical constants an abnormally high ester value and insufficient solubility betrayed the character of the sample; specific gravity was within recognized limits and optical rotation only very little too low: $d_{15°}$ 0.9612, α_D + 8°, acid v. 0.9, ester v. 139.1, soluble in 5 volumes and more of 90 per cent. alcohol. For comparison purposes we may mention that pure oil of calamus is soluble in almost any proportion of 90 per cent. alcohol and possesses a saponification value from 6 to 20. Unfortunately we were unable to determine the kind of ester which had been added, as the quantity of oil submitted for analysis was insufficient, but the comparatively large amount of acetic acid which was separated in the process of saponification points to an acetate having been used; it is probable that the above-mentioned acids were contained in the sample in the form of esters.

Another sample, of the same origin, which was examined by us quite recently, was also found to be adulterated in the most barefaced manner.

G. A. Russell[2]) examined the oils contained in the various parts of the calamus plant. He used partly plants cultivated in Madison (Wis.) as well as ordinary commercial material. The following table gives a resume of the physical and chemical constants of these oils:—

oil from	origin	$d_{23°}$	$[\alpha]_{D28°}$	$n_{D28°}$	acid v.	ester v.	ester v. after acet.
Tops	Madison, Wis.	0.9509	+ 12.2°	1.5035	—	12.6	53.05
rhizomes	Madison, Wis.	0.9547	+ 21.7°	1.4990	—	15.5	38.40
roots	Madison, Wis.	0.9491	+ 18.7°	1.5065	—	23.7	42.10
rhizomes	Bell, Md.	0.9938	—	1.5140	8.15[3])	55.3	—
rhizomes	open market	0.9945	—	1.5080	8.15[3])	42.5	—

[1]) Netherlands East-Indian San Francisco-Committee. Department of Agriculture, Industry and Commerce. No. XXX. Essential Oils. Semarang-Soerabaia-Den Haag 1914. — [2]) *Journ. Americ. Chem. Soc.* **37** (1915), 2387. — [3]) Determined 8 weeks after distillation.

With the plants grown in Madison the yield was 0.123 per cent. from the fresh ærial parts, 0.638 per cent. from dried rhizomes and 2.50 per cent. from dried roots. The air-dried rhizomes from Bell furnished 0.95 per cent. of oil, those of commercial material 1.493 per cent. The yield from the rhizomes cultivated in Madison and Bell is unusually low. This may possibly be due to the fact that the plants had been planted away from their natural surroundings. The oil from the fresh tops was straw-coloured and had a pleasant, aromatic, camphory odour and an acid, spicy, somewhat bitter taste. The oil obtained from the rhizomes grown in Madison and Bell was of reddish-brown colour and possessed an aromatic, somewhat camphor-like odour, resembling that of the freshly dug rhizomes, and a pungent bitter taste. The oil from the roots was golden yellow in colour, had a pleasant camphory odour and a pungent, bitter, acrid taste. From rhizomes obtained in the open market an oil was distilled which had a brownish-yellow colour and also a pungent, somewhat aromatic odour, resembling camphor, and a pungent, bitter taste. The oil from the fresh ærial part of calamus dissolved in 5 and more volumes of 90 per cent. alcohol, with turbidity, and in 18 volumes of 70 per cent. alcohol. Rhizomes grown in Madison yielded an oil which was soluble in 70 and 90 per cent. alcohol. Root oil dissolved in 6 volumes of 90 per cent. as well as in 40 volumes and more of 70 per cent. alcohol. The difference in solubility points to more terpenes or sesquiterpenes being present in root oil than in the oil obtained from rhizomes and ærial parts. The rhizome oil appears to contain more oxygenous bodies than the oil from other parts of the plant. The test for phenols was negative. Aldehydes were proved in all the oils by means of magenta and sulphurous acid, the oil from the tops showing the strongest, root oil the weakest coloration. From this Russell concludes that the formation of aldehydes is more pronounced in the parts of the calamus plant exposed to the light.

In the oil from the tops esterified butyric acid and œnanthylic acid (heptoic acid) were present; they were characterized by the analysis of their silver salts.

The three oils were fractionated by distillation into eight fractions for which the author established the physical constants, as well as their colour and odour. The quantities at his disposal appeared to be too small to permit of the constituents being determined.

Oil of Camphor. According to a British Consular report[1]) on camphor exports from Formosa in 1913 and 1914, the exports rose from 7.86 million pounds of a value of £ 495720.— in 1913 to 8.85 million pounds, of a value of £ 546890.— in 1914. Of these quantities the most important markets received the following shipments:—

	1913	1914
United States	3597000 lbs.	3478000 lbs.
Japan	599000 „	2483000 „
Germany	1048000 „	1464000 „
England	1230000 „	703000 „
France	1374000 „	634000 „
India	— „	72000 „
Austria-Hungary	13000 „	20000 „
total amount:	7861000 lbs.	8854000 lbs.

As will be seen from above table, camphor exports fluctuate considerably. In 1914 Japan drew much camphor from Formosa, but of this quantity it re-exported a

[1]) *Chem. Industrie* 38 (1915), 552.

considerable amount to other countries. There is a noticeable decline in the direct imports of France and England.

The total production of camphor amounted to 6.03 million pounds in 1914 to which has to be added a considerable amount of camphor obtained in the production of camphor oil. A the end of 1914 the stocks of crude and refined camphor were 460000 lbs.

The newly-planted camphor area comprises 3100 acres with 14088457 trees, the total area, however, covered by camphor forests comprises about 1990 English square miles, of which nearly 600 square miles are practically untouched.

In 1914 exports of camphor oil amounted to 4.77 million lbs., value £ 168120.— as against 4.84 million pounds, value £ 172600.— in the preceding year. The production totalled 7.99 million pounds. Stocks of camphor oil amounted to about 721000 lbs. at the end of the year.

From the *Japan Chronicle*[1]) we gather that the number of orders for camphor received at the beginning of the year from America was particularly large. Furthermore the journal *The Asahi* states that the firm of Suzuki & Co. alone has booked American orders to the extent of 300000 lbs. In consequence of this heavy demand prices rose to 69 and 70 yen. Moreover, the above firm received Russian orders to the extent of 85000 lbs. for early February, 10000 lbs. for middle of March and 10000 lbs. for late March, later orders amounting to 440000 lbs. It will be understood that under the circumstances the camphor market is very brisk.

The Monopoly bureau estimates the quantities of camphor brought into the market this year at 4050000 kin, *i. e.* 1200000 less than last year. As, however, an ever-increasing demand will have to be reckoned with, dealers will petition the Government to allow larger quantities to be brought into the market.

At the Imperial Institute in London[2]) two samples of camphor oil obtained by decantation and expression from crude camphor of the Japanese camphor tree *(Cinnamomum Camphora)* were examined. The samples were freed from camphor as far as possible by cooling, and the following constants established: d_{15° 0.913 and 0.920; α 41° 1′ and 38° 23′ (+ ?); acid v. (sample II) 1.1; sap. v. 3.6; after acet. 25.7. Oil II was fractionated, when it was found that, calculated on the original oil, it contained 4.3 per cent. cineole and 30.5 per cent. camphor. Safrole was absent, probably because the original distillate was obtained from young twigs and leaves whereas commercial Japanese camphor is derived from old wood of mature trees.

On page 9 of our *Report* October **1915** we mentioned that in Satsuma Heights (Florida) 10000 lbs. of crude camphor had been obtained in the previous year. A considerably larger crop is anticipated next year[3]). It appears that more than 2000 acres have been planted with camphor trees and it is expected that 500 additional acres will be set during the winter. Other smaller plantations in different parts of the State will shortly come into bearing and many others will soon be set out. Besides, countless small farmers and truck growers appear to have grown a few rows of these valuable trees around their fields, and these will count sooner or later in the production of camphor.

We take it that this note deals with camphor to be obtained from the leaves; nothing can be gathered concerning this point from the article referred to.

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[1]) *Handelsberichten (Den Haag)* **10** (1916), 258. — [2]) B. J. Eaton, *Agr. Bull. Fed. Malay States* **3** (1915), 402; *Journ. Soc. Chem. Industry* **35** (1916), 274. — [3]) *Scientific American; Midland Drugg. and Pharm. Review* **49** (1915), 408

In a paper on natural and artificial camphor P. A. Houseman[1]) discusses the methods of production and sublimation, the chemistry as well as the properties and history of these articles, without, however, contributing anything new. There is not, therefore, any occasion for anything but this reference.

Oil of Cananga. The qualities of cananga oil placed on the European market from time to time are best illustrated by a sample submitted to us for analysis by an importing firm recently. The constants were as follows: d_{150} 0.8973; α_D — 8° 18′; sap. v. 61.5; insoluble in 95 per cent. alcohol from the very start; separation of oil at the bottom of the tube.

Not one of the above-mentioned constants is within the limits recognized for cananga oil; specific gravity and optical rotation are much too low, saponification value is too high and, moreover, solubility is quite unsatisfactory. As a closer investigation proved, these irregularities were due to the oil having been heavily adulterated, the presence of coconut oil having been established beyond doubt. On rectification by steam there was a residue of 18.3 per cent. which became solid at ordinary temperature, showing a saponification value of 241.7, a figure which characterized it as coconut oil. Seeing that pure cananga oil leaves but 3 per cent. of residue under ordinary circumstances, the quantity of coconut oil added should be somewhere near 15 per cent.

In face of the low specific gravity of the sample under examination it was evident that coconut oil was not the only adulterant used, for this oil alone could not depress the specific gravity down to 0.8973, as it is specifically heavier itself. Unfortunately it was impossible to investigate the sample more closely, the quantity at our disposal being insufficient for further analysis.

Oil of Caraway. According to the report of the Netherland Ministry of Agriculture of the 15th. of July, 1916, the area under caraway cultivation this year amounts to 5032 hectares[2]) against 3967 hectares in 1915

„ 5285 „ „ 1914

and 5527 „ „ 1913

The report on the state of the plantations was good for Groningen and Northern Holland, fair to good for Southern Holland and fairly good for Zealand and Northern Brabant. No more recent reports are to hand. Caraway prices have undergone an extraordinary rise in the course of last spring, the quotations of about fl. 26.— given at the end of last year rising to a level of fl. 46.— per cwt. in May, a figure never reached before. Caraway oil prices rose accordingly and although very considerable stocks of oil were available in Germany, quotations had to follow suit. At the present time the market is fairly quiet. If the weather were to be propitious during the harvest and the yield of oil not below the average (in 1915 it was well below the average) the result of the distillation would help towards bringing back normal conditions, for the area under cultivation is nearly as large as in 1914. The demand from Germany and Austria will probably remain small for caraway and caraway oil, seeing that the liqueur industry is well nigh paralyzed through want of sugar and spirits of wine. It cannot be said with certainty whether the export prohibition for caraway introduced by the Netherland Government will remain in force after the new crop.

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[1]) *Americ. Journ. Pharm.* 87 (1915), 49. — [2]) 1 Hectare equals about 2½ acres.

Oil of Cardamoms. More cardamoms were exported from Ceylon in 1915 than in the preceding year[1]), as will be seen from the table below, shewing the exports during 1914 and 1915:—

Ceylon Cardamom exports during 1914 and 1915.

Destination	1914	1915
Great Britain	210916 lbs.	330562 lbs.
France	5937 „	5380 „
Germany	52766 „	— „
Denmark	3240 „	— „
Russia	1536 „	— „
Sweden	9991 „	— „
Turkey	7545 „	— „
United States	62289 „	137662 „
Egypt	4960 „	16370 „
India	15155 „	18719 „
Straits Settlements	967 „	2458 „
Japan	— „	3186 „
China	— „	3849 „
Total:	376321 lbs.	519039 lbs.

Oil of Cassia. Owing to the readiness with which cinnamaldehyde oxidises, cassia oil almost always contains traces of free cinnamic acid which is unpleasant inasmuch as it attacks the leads in which the oil is packed, the oil becoming contaminated with lead in consequence. For commercial and medicinal purposes it is therefore recommended to use rectified cassia oil only, which is free from lead.

As experiments carried out in our laboratories have proved, lead can be removed without difficulty by shaking the oil with tartaric acid. One gram of the powdered acid is added to 100 grams of oil, the whole is shaken repeatedly and thoroughly and allowed to stand for 24 hours when the flocculent deposit is removed by filtration. Oils which gave a very positive lead reaction (shaking a few drops of oil with water containing sulphuretted hydrogen, when the oil drops become coloured red or black, according to the quantity of lead present) showed no trace of lead after above treatment. Moreover, the colour of the oil had become much lighter and in determining the aldehyde percentage a further advantage was noticeable. For, whereas an exact reading-off of the non-aldehydic contents in the original oils, containing lead, was practically impossible on account of the heavy crystalline separation noticeable at the division line of oil and aqueous solution, this could be done with every degree of correctness after the oil had been shaken with tartaric acid prior to the aldehyde test, for crystalline separations had then practically disappeared.

As the process is extremely simple and entails practically no loss of oil, it will be found especially suitable for treating small quantities of oil and should therefore be of particular interest to the chemist and the druggist.

In the course of an examination of a sample of cassia oil F. D. Dodge and A. E. Sherndal[2]) observed that, when the alkaline solution obtained by shaking the oil with dilute sodium hydroxide was acidified and distilled with steam, the distillate gave

[1]) *Chemist and Druggist* 88 (1916), 382. — [2]) *Journ. Ind. Eng. Chemistry* 7 (1915), 1055.

an intense purple coloration with ferric chloride. On submitting a number of oils to similar treatment it was found that all gave a similar reaction. This proved that cassia oil contained hithertofore unknown phenol-like constituents, for the bodies found in the oil so far did not give the colour reaction with ferric chloride. In order to isolate these phenols 500 grams of a freshly rectified oil of undoubted purity were treated. The constants were: $d_{25°}$ 1.050; α_D + 0.32°. Cinnamaldehyde 88 per cent. It was extracted twice with 500 cc. portions of 2 per cent. sodium hydroxide, and the clear alkaline solution acidified and extracted with ether. The ether solution was then shaken with 10 per cent. sodium bisulphite solution, the latter neutralized with soda, distilled with steam and the distillate again extracted with ether. The ether solution, on evaporation, left a colourless oil weighing 1.66 grams, showing the characteristic properties of salicylaldehyde and yielding a crystalline semicarbazone melting at 228° with decomposition.

The first ether solution, after extraction with bisulphite, was washed with sodium bicarbonate solution to remove acids and then evaporated. An oily residue, weighing 0.53 g. was obtained which crystallized on standing and was identified as coumarin. After crystallization from hot water it melted at 67°. From the bicarbonate washings a small amount of a crystalline acid was isolated which melted at 123 to 128° and proved to be cinnamic acid (acid v. 379, calculated 378.3). As further constituents soluble in alkali appeared to be present, 600 lbs. of cassia oil were treated with alkali, when 3 lbs. were dissolved. Of this about 25 per cent. was readily volatile with steam, and consisted principally of salicylaldehyde, the balance containing coumarin and an oily acid showing a molecular weight of about 175. A larger quantity of this acid, or acid mixture, was isolated from the portion of oil not easily volatile with steam. In the crystalline part of this mixture there was coumarin, besides salicylic acid, the liquid part contained the oily acid mixture referred to. When esterified it yielded an ester mixture having the characteristic odour of the esters of the higher fatty acids and consisted of parts lighter than water, as well as parts heavier than water, the latter apparently containing ethyl benzoate.

The result of the examination showed that cassia oil contains at least 0.5 per cent. of bodies soluble in dilute alkali, consisting of a mixture of about 25 per cent. of salicylaldehyde, 60 per cent. coumarin, 8 to 10 per cent. cinnamic acid and small amounts of salicylic acid, benzoic acid and a volatile liquid acid not identified.

The presence of small amounts of salicylaldehyde and of coumarin is undoubtedly of importance for the odour of cassia oil. It is remarkable that salicylaldehyde which in the process of fractionation can be detected by its odour in the first parts, should so long have escaped observation.

On page 92 a few notes will be found on a colorimetrical method of determining cinnamaldehyde.

Oil of Celery. According to A. Juillet[1]) the celery seed cultivated in Provence and Anjou is used principally in the manufacture of celery essence (concentrated bouillon). The chief places of export are St. Remy de Provence and Marseilles, the total quantity amounting to about 250 to 300 tons at prices ranging from fr. 35.— to fr. 200.— per cwt. The germinating capacity of the seed is on an average about 70 per cent. Among the impurities mineral substances, stems, leaves, extracted as

[1]) *Annal. Falsific.* **6** (1913), 671; *Zeitschr. Untersuch. d. Nahrungs- u. Genussm.* **31** (1916), 368.

well as other seeds are mentioned. With ordinary seeds of commerce the content of impurities is hardly ever less than 3 per cent. The worst adulterations are coloured mineral substances and admixtures of extracted seed. Mineral substances are best recognized by shaking from 3 to 5 g. of the seed with 100 cc. of carbon tetrachloride. Exhausted seed, when examined under the microscope, betrays its presence mostly by its darker colour, its rounded edges and moreover by its lack of germinating capacity and its comparative power of resistance against fungoid growth in the germinating bed. A certain proof of their presence is based on the fact that in normal seed the beautifully regular, egg-shaped aleuron grains fill the cells without leaving any interstices, whereas with extracted seed the outlines of the granules are irregular and torn, leaving big hollow spaces between the individual grains. The determination of the percentage of volatile oil yields useful indications only in the event of a very considerable percentage of extracted seed having been admixed.

Oil of Chrysanthemum cinerariæfolium[1]). From 30 kilos of Dalmatian pyrethrum blossoms (insect powder) P. Siedler[2]) obtained by steam distillation 20.212 g. = 0.067 per cent. of a salve-like mass having a strong, peculiar, aromatic odour. The mass was spread on a porous tile and allowed to stand for 24 hours when the parts adhering to the surface (0.789 g. = 3.9 per cent.) were scraped off. From this product two bodies could be isolated, a paraffin $C_{14}H_{30}$, melting at 54 to 56° and an acid, melting at 62°, possibly palmitic acid. The tile was extracted with ether in the Soxhlet apparatus. From the concentrated solution a substance was separated which melted at 62°. By means of bisulphite solution traces of an odoriferous substance were obtained from the parts absorbed by the tile, which appeared to have no effect on insects. The oil freed from aldehyde- and ketone-like parts contained traces of phenols which, however, could not be further investigated as the material under examination was too limited. Even the acid parts isolated from the oil, which smelled like butyric acid, did not affect insect life. The oil which remained after removal of acids and phenols was acetylated, when a substance smelling like cresol was obtained. This may have been a phenol.

Siedler's investigations establish the fact that the insecticide properties of insect powder are not due to the volatile oil of the plant.

Oil from the leaves of Cinnamomum pedunculatum. From the green leaves of *Cinnamomum pedunculatum* (N. O. *Lauraceæ*)[3]), a native of Japan, V. Shenosaki[4]) obtained by distillation 1 per cent. of a brown oil the odour of which reminded of camphor. $d_{15°}$ 1.0603; α_{D200} — 1.75°; acid v. 0; ester v. 5.6; ester v. after acet. 25.25. The oil contained 9 per cent. of hydrocarbons and cineole, 3 per cent. eugenol, 60 per cent. safrole and 28 per cent. of other oxygenous constituents. From the note in question it does not appear as to how the presence of these bodies was proved.

Oil of Cinnamon, Ceylon. Induced by the scarcity of cinnamon oil prevalent in England, the London Imperial Institute has been in communication with the Ceylon Agricultural Society with a view to ascertaining whether distillation of cinnamon bark

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[1]) See Gildemeister und Hoffmann, *Die ätherischen Öle*, 2nd. ed., vol. III, p. 677. — [2]) *Berichte d. deutsch. pharm. Ges.* **25** (1915), 279. — [3]) So far only the bark oil of this species of Cinnamomum was known. See Gildemeister and Hoffmann, *The Volatile Oils*, 2nd. ed., vol. II, p. 446. — [4]) *J. Chem. Ind. Jap.* **18** (1915), 913; *Chem. Abstr. Americ. Chem. Soc.* **10** (1916), 370. From *Perfum. Record* **7** (1916), 64.

could be taken up once again in Ceylon[1]). It would be of interest for the importers of Ceylon cinnamon oil to get into touch with producers of cinnamon oil resident in Ceylon, for which purpose the director of the Imperial Institute asked for price and quantity of oil available for shipment. He added that for certain purposes it is of importance that importers should be in a position to guarantee the oil to be genuine, *i. e.* that it consists of oil only obtained by distillation of the cinnamon bark and that it is not adulterated with cinnamaldehyde, cassia oil, or any other substance. The secretary of the Lowcountry Products Association reported that distillation of cinnamon bark oil had been given up some years ago in consequence of the low prices realized and owing to the greater demand for cinnamon leaf oil. Also, that it was improbable that it would be taken up again unless a very brisk demand for pure bark oil were to set in and that trade in chips were to decline at the same time to a considerable extent. From another quarter the reply was obtained that oil which sold at a price of about Rs. 1.25 to 1.50 per oz. was undoubtedly mixed with leaf oil but that at prices ranging from Rs. 3.— to 3.50 a pure distillate was obtainable. Still another source states that no unadulterated cinnamon bark oil was exported fron Ceylon because it was too dear and demand was not important enough. The product exported as cinnamon bark oil usually contained 50 per cent. and more of cinnamon leaf oil. It was stated that if of late years pure cinnamon oil had been exported to England from Germany, this oil would have been distilled in Germany from imported chips. Another correspondent writes to the effect that the market for this oil was flat, that Ceylon oil was hardly ever pure and that it contained from 10 to 20 per cent. of leaf oil.

Finally the secretary of the Lowcountry Products Association reported on his negociations with parties interested in the cinnamon industry and declares that it would be possible to provide English buyers with about 1000 oz. of cinnamon bark oil monthly, and that the price would be from Rs. 2.25 to 3.— per oz. A sample of one lb. was distilled for the Association and was examined by the Government Agricultural analyst whose report is as follows: α 1°, aldehyde content 68 per cent., eugenol content 16 per cent. As will be seen, the eugenol content is fairly high so that it is not impossible that the sample examined was not pure either.

In 1915 Ceylon exported

4 123 433 lbs. of cinnamon bark and 2 045 287 lbs. of chips
as against 2 361 994 „ „ „ „ „ 1 498 464 „ „ „ in 1914.

Of cinnamon chips 280 870 lbs. went to Great Britain, 57 828 lbs. to the United States and 213 860 lbs. to Spain in 1915[2]).

On the exports of cinnamon bark from the Seychelles see page 91 of this *Report*.

On a colorimetric method of determining cinnamaldehyde compare Analytical Notes, page 92.

Oil of Citronella. Exports from Ceylon were greater in 1915 than in 1914, as will be seen from the table below[2]).

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[1]) *Perfum. Record* 7 (1916), 5. — [2]) *Chemist and Druggist* 88 (1916), 382.

Destination	1914	1915
Great Britain	596897 lbs.	464070 lbs.
France	27089 „	88539 „
Germany	99655 „	— „
Australia	108082 „	105209 „
United States	529443 „	899001 „
India	12539 „	15092 „
Straits Settlements	2500 „	270 „
Japan	21501 „	32167 „
China	28237 „	34547 „
Total:	1425943 lbs.	1638895 lbs.

In a pamphlet issued by the Netherlands East-Indian San Francisco Committee[1]) we find the following statistical notes on the exports of citronella oil from Java in 1912 and 1913[2]).

The total exports amounted to 169459 lbs. in 1912 and to 166070 lbs. in 1913, distributed as under: —

Destination	1912	1913
Holland	30367 lbs.	22609 lbs.
Holland f/t[3])	7510 „	22472 „
France	14732 „	46660 „
Germany	75089 „	52592 „
other parts of Europe	555 „	5982 „
United States	37112 „	14651 „
other countries	4094 „	1104 „
Total:	169459 lbs.	166070 lbs.

Oil of Cloves. J. Hortvet[4]) published a communication on experiments about direct determination of volatile oil in cloves, by means of distillation in a current of steam. In this he starts from experiments made by Reich[5]) whose method he modifies slightly by using a special apparatus[6]). Hortvet's apparatus consists of a flask of 350 cc. capacity, in the neck of which a cylindrical flask of 75 cc. capacity is introduced which is fitted with a siphon-like side-tube. The smaller flask can be joined to a condenser. For distillation purposes 2 g. of cloves are placed in the inner flask along with 25 cc. of 20 per cent. salt solution, and 250 cc. of salt solution in the outer flask. The apparatus is then closed and connected with the condenser. When the liquid in the outer flask has reached boiling point, the steam is forced through the mixture of cloves and salt water in the inner vessel, and distillation is continued until 225 cc. of the distillate have been collected. The distillate is next shaken in the separatory with 35, 25, 15 and 10 cc. of ether successively, the united ether extracts are washed in water, the ether is filtered and evaporated in a tared vessel. The results thus obtained are from 0.24 to 2.78 per cent. lower than those obtained by the official (American) method of extraction, in which process the total ether extract is first determined, after which the volatile ether extract is ascertained. In judging cloves it

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[1]) Netherlands East-Indian San-Francisco Committee, Department of Agriculture, Industry & Commerce, No. XXX. Essential Oils. Semarang-Soerabaia-Den Haag 1914. — [2]) See *Report* October **1913**, 41. — [3]) f/t — for transit (*i. e.* re-export). — [4]) *Americ. Perfumer* **10** (1915), 257 and *Journ. Soc. Chem. Industry* **34** (1915), 1164. — [5]) *Zeitschr. Untersuch. d. Nahrungs- u. Genussm.* **18** (1909), 401; *Report* April **1910**, 43. — [6]) *Journ. Ind. Eng. Chemistry* **1** (1909), 31.

goes without saying that the results obtained by one method cannot, on any account, be compared with those obtained by the other method.

A. W. Ogden[1]) reports on the loss in weight sustained by cloves when stored. The result of his investigations was that with seven samples he ascertained an average loss, after six months, of 2.42 per cent. and he found that after 54 months the average loss was 4.70 per cent. The greatest decrease in weight amounted to 7.83 per cent.

Oil of the leaves of Cryptomeria japonica. The conifer *Cryptomeria japonica*, Don., known by the name of "Sugi", is a native of Japan where it is planted on a large scale on account of its wood. The oil from the wood has been examined[2]) repeatedly whereas the oil from the leaves has only been described by So Uchida quite recently[3]). By distilling green leaves he obtained 0.7 per cent. of a brownish-yellow, readily mobile oil which boiled at ordinary pressure from 155 to 350°. The constants were as follows: $d\frac{15.5°}{15.5°}$ 0.9217; $[\alpha]_{D15°}$ 19.29°[4]) (10 per cent. solution in chloroform); $n_{D20°}$ 1.4895; acid v. 1.0; ester v. 6.56; after acet. 14.35. By means of soda solution a small quantity of free acid was separated from the oil but it was not sufficient for closer investigation. In the low-boiling parts of the oil *d*-α-pinene was found: nitrolpiperidine, m. p. 118 to 119°, nitrolbenzylamine, m. p. 122 to 123°. β-Pinene could not be proved, but dipentene was identified by means of the tetrabromide, m. p. 123 to 124°. The parts boiling between 100 and 180° (15 mm.) were examined after acetylation, when it was found that they contained an alcohol $C_{10}H_{18}O$, boiling at 213 to 214°; $d\frac{18°}{18°}$ 0.9414; $[\alpha]_D$ + 56.07° (8.98 per cent. solution in chloroform); $n_{D18°}$ 1.4832. The alcohol could not be completely acetylated. Its odour resembles camphor as well as peppermint and seems to be of importance for the aroma of the oil. From the high-boiling parts of the oil a twice unsaturated sesquiterpene $C_{15}H_{24}$ was isolated, b. p. 266 to 268°; $d\frac{15.5°}{15.5°}$ 0.9335; $[\alpha]_D$ + 15.19° (6.08 per cent. solution in chloroform); $n_{D22.8°}$ 1.5041. It yielded a liquid dihydrochloride; solid derivatives, such as nitrosochloride, nitrosite, nitrosate, bromide, or hydrate, were not obtained. Cadinene was present in a fraction boiling from 272 to 275°; it formed a dihydrochloride, m. p. 117 to 118°[5]). Furthermore the oil contained a sesquiterpene alcohol $C_{15}H_{26}O$, b. p. 284 to 286°; $d\frac{15.5°}{15.5°}$ 0.9623; $[\alpha]_{D15°}$ + 16.76° (5 per cent. solution in chloroform); $n_{D22.8°}$ 1.5048. The sesquiterpene alcohol was distilled from a fraction b. p. 270 to 280°, which was of dark blue colour and may have contained azulene. The fractions boiling from 180 to 200° (15 mm.) contained, moreover, an unknown diterpene $C_{20}H_{32}$, the α-cryptomerene; m. p. 61°; b. p. 198° (15 mm.); 345° (ord. pressure); $[\alpha]_{D20°}$ — 34.32° (4.69 per cent. solution in chloroform). As it adds no iodine it may be looked upon as a saturated body. It yields no crystalline derivative with bromine. Even when treated with concentrated sulphuric acid no characteristic compound resulted; on the other hand treatment with hydrochloric acid gas changed it to an isomeride of the m. p. 211 to 212°, *i. e.*, β-cryptomerene. From the saponification liquor of the oil Uchida obtained a body $C_{20}H_{32}O_2$, evidently a lactone, as well as caprylic acid (analysis of the silver salt).

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[1]) *Americ. Journ. Pharm.* **87** (1915), 526. — [2]) See Gildemeister and Hoffmann, *The Volatile Oils*, 2nd. ed., vol. II, p. 137. — [3]) *Journ. Americ. Chem. Soc.* **38** (1916), 867. — [4]) The direction of the rotation is not given. — [5]) On page 49 of our *Report* April **1914** we pointed out that the isolation of cadinene hydrochloride by itself could no longer be regarded as a proof of the presence of cadinene, as besides cadinene there are two other sesquiterpenes which yield cadinene hydrochloride when treated with hydrochloric acid gas.

The quantitative composition of the oil is approximately as follows: 34 per cent. of terpenes (chiefly dipentene), 30 per cent. sesquiterpenes (chiefly the sesquiterpene of the b. p. 266 to 268°), 4.5 per cent. alcohols $C_{10}H_{18}O$, 18 per cent. cryptomerene and 12 per cent. sesquiterpene alcohol.

Oil of Cymbopogon sennaarensis. The grass *Cymbopogon sennaarensis*, Chiov. is known by the name of "mahareb" in the British Soudan. The oil had been described by the Imperial Institute in London some years back[1]), but a closer investigation was only carried out recently by O. D. Roberts[2]). In odour the herb resembles oil of pennyroyal, but it smells stronger. On distillation of a small parcel of the herb, about 1 per cent. of oil was obtained at the time; $d_{15°}$ 0.9383; $\alpha_{D20°}$ + 34° 14′; sap. v. 14; ester v. after acet. 60.2. In 1912 a larger parcel of grass was distilled, the yield being 1.2 per cent. $d_{15°}$ 0.9422; $\alpha_{D23°}$ + 29° 38′; acid v. 4.2; ester v. 14.5; after acet. 62.1. The oil contained presumably *n*-octylic, decylic and acetic acid in the free state and probably esterified octylic, decylic and palmitic acids (m. p. 62.6°); 45 per cent. of the oil reacted with sodium sulphite or sodium bisulphite. The substance recovered from the bisulphite compound by means of sodium hydroxide proved to be identical with Δ^1-menthenone which was produced synthetically by Wallach some years ago[3]) and was found by us later in Japanese peppermint oil[4]) and in camphor oil[5]).

The constants of these three preparations are as follows:—

Origin of Δ^1-menthenone:	b. p.	d	α_D
from the oil of *Cymbopogon sennaarensis*	235 to 237°	0.9387 (15°)	+ 1° 44′ at 22°
from Japanese peppermint oil	235 to 237°	0.9382 (15°)	+ 1° 30′
synthetical	235 to 237°	0.9375 (19°)	inactive.

The semicarbazones obtained from the *Cymbopogon* menthenone, the oxime and oxamino-oxime, showed the melting points indicated by us. The *bis*nitroso compound of Δ^1-menthenone formed hard white crystals, m. p. 96 to 97°. By oxidation with neutral 2 per cent. potassium permanganate solution Roberts obtained the two bodies also found by us, *viz.*, *γ*-acetyl-*α-iso*propylbutyric acid and *α*-hydroxy-*α*-methyl-*α′-iso*-propyladipic acid, as well as diosphenol (m. p. 82°) and another acid, not further investigated, of the m. p. 126 to 127°. By reduction with sodium and alcohol the Δ^1-menthenone furnished menthol (phenylurethane, m. p. 111 to 112°).

The oil also contained 0.2 per cent. of phenols, from which a benzoyl compound of the m. p. 70 to 72° was isolated; lack of material prevented the phenol being more closely investigated. After elimination of menthenone and of the phenols an oil remained which, after acetylation, had the specific gravity $d_{15°}$ 0.9422; $\alpha_{D22°}$ + 21° 21′. Of terpenes, Roberts proved *d*-limonene (tetrabromide, m. p. 103 to 104°) to be present in this fraction. Pinene (b. p. 153 to 163°; $d_{15°}$ 0.865; $\alpha_{D22°}$ + 65° 15′) also seems to be present, but no nitrosochloride could be obtained. By means of phthalic anhydride an alcohol with a rose-like odour was obtained from the acetylated oil, upon oxidation with chromic acid it furnished a body smelling like tanacetone. The high-boiling parts of the saponified oil contain a sesquiterpene alcohol $C_{15}H_{26}O$, b. p. 170 to 175° (21 mm.); 280 to 285° (ordinary pressure); $d_{15°}$ 0.9544; $\alpha_{D24°}$ + 10° 48′. Quantitative acetylation was impossible. Splitting off water by means of phosphoric pentoxide led to a ses-

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[1]) *Bull. Imp. Inst.* **10** (1912), 27; *Report* October **1912**, 52. — [2]) *Journ. Chem. Soc* **107** (1915), 1465. — [3]) *Liebigs Annalen* **362** (1908), 272; *Report* October **1908**, 181. — [4]) *Report* October **1910**, 97. — [5]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd. ed., vol. II, p. 463.

quiterpene of the b. p. 150 to 155° (27 mm.); $d_{15°}$ 0.9114; $\alpha_{D23°}$ +24°24′. The quantitative composition of the oil is approximately as under: 13 per cent. terpenes, 45 per cent. Δ^1-menthenone, 25 per cent. sesquiterpene alcohol, 3 per cent. alcohol with rose-like odour, 0.2 per cent. phenols, 2 per cent. acids and 11.8 per cent. residue, in the main presumably sesquiterpenes.

Oil of Cypress. Considering that this oil is chiefly, if not exclusively, used for therapeutical purposes, its purity is of particular importance. This consideration induces us to give a few notes on an oil originating from France, and submitted to us for analysis by a Swiss firm. Though the constants were in order ($d_{15°}$ 0.8912; α_D +12°55′; acid v. 0.6; ester v. 11.2; soluble in 1 volume and more of 90 per cent. alcohol), the odour of the oil resembled rosemary oil more than cypress oil, so that from the very first we entertained little doubt but that we had to deal with a heavily adulterated oil the constants of which had been adjusted to resemble cypress oil.

This case deserves special mention because genuine cypress oil and its therapeutical value might be seriously injured, for it was evident that the buyer was inclined to rely on the quality of the oil, the more so as it came from France, that is from the country in which the cypress tree occurs and where, therefore, the procuring of raw material offers no difficulties in spite of the war.

Oil of Datura Stramonium. From the dry leaves of the common thorn-apple (*Datura Stramonium*, L., N. O. *Solanaceæ*) H. Hænsel[1]) had obtained some time ago a dark brown oil smelling of tobacco; his report only deals with the properties of this product, but gives no indications as to its composition. Further informations on the odoriferous constituents of the thorn-apple are found in a paper by A. Sivolobov[2]) who, by distilling stems, leaves, flowers and other parts of the plant with water, obtained a mixture of methyl alcohol, ethyl alcohol, trimethylcarbinol (?), aldehydes, ketones and esters. Among the aldehydes he found acetaldehyde and presumably also formaldehyde, propylaldehyde, *iso*butaldehyde, and another aldehyde of a higher boiling point. Furthermore, acetone was found and a high-boiling ketone, as well as acetates and formates. In the process of distilling the herb a gas is developed, consisting of carbon dioxide and of a poisonous, odoriferous gas which is not absorbed by potash lye and which is perhaps identical with formaldehyde. The note does not give any indications as to the manner in which these bodies were proved.

Oil of Elemi. On the occasion of an experiment to produce elemicin from Manila elemi oil ($d_{15°}$ 0.9096; α_D +35°43′), we obtained, in place of the liquid elemicin, a fraction which became solid and from which, when cooled with a little alcohol followed by light petroleum, we obtained a body of the m. p. 51 to 52°. The elemi used for the purpose was the usual commercial quality obtained from Hamburg. An enquiry with the importing firm elicited the information that the gum had been collected in the usual way in the Philippine Islands, but that no particulars could be given as regards botanical origin. According to R. F. Bacon[3]) only *Canarium luzonicum*, (Miq.) A. Gray need be considered as mother-plant of Manila elemi. The many other *Canarium* species supply either a different kind of gum or else such small quantities of elemi-

[1]) *Chem. Zentralbl.* **1910**, II. 1539. — [2]) *Journ. russ. phys. chem. Ges.* **47** (1915), 1561; *Chem. Zentralbl.* **1916**, II. 227. — [3]) *Philippine Journ. of Sc.* **4** (1909), A, 93.

like substance, that it does not pay to collect them. We may take it that the material used by us at the time contained not only the gum from *Canarium luzonicum*, but admixtures of other kinds as well.

The fraction which becomes solid was examined by F. W. Semmler and Futung Liao[1]). It had the following constants: boiling point 143 to 146° (12 mm.); $d_{20°}$ 0.9638; α_D slightly dextrorotary; n_D 1.5037 (undercooled). Elementary analysis yielded figures which did not quite agree with a sesquiterpene alcohol, nor with a compound $C_{15}H_{24}O$. It may therefore be assumed that the authors had to deal with a mixture of a sesquiterpene alcohol, $C_{15}H_{26}O$, with elemicin, $C_{12}H_{16}O_3$. By means of benzoyl chloride and pyridine the sesquiterpene alcohol was converted into its benzoate which boiled at 214 to 218° (10 mm.); $d_{20°}$ 1.0287; α_D — 6°; n 1.5378. The sesquiterpene alcohol $C_{15}H_{26}O$ was obtained from the benzoate by saponification: b. p. 152 to 156° (17 mm.); $d_{20°}$ 0.9411; α_D — 5°; n_D 1.5030. The authors designate the alcohol *elemol*. To judge from the molecular refraction (found 69.73, calculated for $C_{15}H_{26}O/\overline{2}$ 69.77) it can only be a question of a monocyclic, doubly unsaturated alcohol. This is the first time that a monocyclic sesquiterpene alcohol has been established in nature, though monocyclic sesquiterpenes have been observed before now. By dehydration by means of potassium bisulphate, formic acid, and zinc sulphate to which zinc dust had been added, practically the same result was obtained in all cases. In splitting off water with formic acid, a monocyclic sesquiterpene was formed with three double linkings, probably mixed with some bicyclic sesquiterpene. The constants of the monocyclic sesquiterpene were as follows: b. p. 115 to 117° (10 mm.); $d_{20°}$ 0.8797; α_D to the right; n_D 1.4971; molecular refraction found 67.84; calculated for $C_{15}H_{24}/\overline{3}$ 67.86. The sesquiterpene was called *elemene*. Elemene cannot be reduced by means of sodium and alcohol, from which it follows that it probably does not contain any conjugated double linkings. On reduction with hydrogen and platinum in ethereal solution it formed a hydrocarbon $C_{15}H_{30}$, hexahydroelemene, of the boiling point 114 to 116° (10 mm.); $d_{20°}$ 0.8450; $[\alpha]_D$ — 4.8°; n_D 1.4621; molecular refraction found 68.35, calculated for $C_{15}H_{30}$ 69.04. The difference between the calculated refraction and the refraction actually found may possibly be due to a slight admixture of a bicyclic compound. Elemol also does not appear to possess a conjugated double linking, as it is reduced neither by sodium nor alcohol. By means of platinum and hydrogen it was readily reduced to tetrahydroelemol, $C_{15}H_{30}O$, from which tetrahydroelemene $C_{15}H_{28}$ is formed by means of dehydration. Boiling point 117 to 119° (10 mm.); $d_{20°}$ 0.8659; α_D — 20.4°; n_D 1.4760. This tetrahydroelemene, when reduced with platinum and hydrogen, yielded a hexahydroelemene which practically corresponded with the hexahydroelemene described above.

From time to time elemi-like products appear in commerce which are usually called after the country they come from. Thus the gum of *Dacryodes hexandra* is called West Indian or Dry elemi, whereas in the West Indies it is known by the name of *Gommier resin*. Aromatic oil-gums from different parts of Western Africa are sometimes called West African elemi, such as Liberia, Cameroons and Southern Nigeria elemi[2]). Formerly elemi resin was used in considerable quantities for medicinal purposes, as an addition to ointments and plasters; to-day this is hardly the case any longer, it being used principally in the manufacture of printers' ink and occasionally as an addition to varnishes. The comparatively small demand appears to be easily covered by the quantities obtained in the Philippine Islands.

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[1]) *Berl. Berichte* 49 (1916), 794. — [2]) Gildemeister und Hoffmann, *Die ätherischen Öle*, 2nd. ed., vol. III, p. 139.

A new kind of elemi is the one from *Canarium Colophania*[1]) occurring in Mauritius. In appearance and odour it shows a great similarity with the Manila elemi of commerce. It contains 16.6 per cent. of a straw-coloured volatile oil of lemon-like odour and showing the following properties: $d\frac{15.5°}{15.5°}$ 0.859; $[\alpha]_D + 3°13$; n_D 1.4725.

Essential Oils, Sicilian and Calabrian.

In an exhaustive article R. T. Will[2]) reports on the development and the present state of the Citrus by-product industry in California, by which is understood the utilization of lemons and oranges, unfit for export, in the manufacture of useful by-products, such as essential oils, marmelades, fruit juices, candied peel and citric acid. A capital of $ 175 000 000.— has been invested in this industry. Annually 38 000 carloads of oranges and 6000 cars of lemons and grape fruit representing a total of 1 232 000 000 lbs. of citrus fruit are grown and shipped to eastern markets. Only the best fruit is selected for these markets and the "cull" fruit[3]) is used in the manufacture of citrus by-products. According to Mc Dermott the amount of "culls" may reach 10 per cent. in unfavourable years in Florida. It is estimated that in California from 1 to 5 per cent. of the total shipments of fruit are available for the manufacture of citrus by-products, *i. e.* about 12 320 000 to 61 600 000 lbs. It is evident that such an enormous quantity of discarded fruit must be made use of. The simplest plan would appear to be the manufacture of marmelade; but this would cost as much, or more, as the imported article, and moreover it has not, as will be shewn further on, the valuable properties of English marmelade so much appreciated by the public.

Commercial manufacture of citrus by-products was started in National City in 1899 where a rather extensive plant for the manufacture of oil of lemon, citrate of lime and citric acid was erected. After operating but a short time, it had to be closed for lack of sufficient capital and for certain other reasons, the principal one of which appears to have been the indifferent quality of its lemon oil, which sold 50 cents cheaper than the imported article, also on account of the inferior quality of citric acid and considerable losses in the process of manufacture. Shortly after this plant had closed down, the newspapers started a tremendous advertisement campaign for Los Angeles as the coming seat of an enormous industry, the citrus by-product. The product to be made there was lemon juice preserved with all its original characteristics for household and numerous other uses. It was surprising to learn that lemon juice not only promoted the growth of the hair but it could also be used, with the proper mixture of other ingredients, as a furniture polish.

Several car-loads of lemon juice were packed in bottles of various sizes and shipped to eastern points where it met with considerable success. Unfortunately after a few weeks on the shelves of the stores it spoiled and the company found itself saddled with thousands of bottles. This happened over ten years ago and up to this day the problem of preserving lemon juice is not completely solved.

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[1]) *Bull. Imp. Inst.* **13** (1915), 374. According to the Index Kewensis *Canarium mauritanicum*, Blume is synonymous with *Canarium Colophana*, Baker. — [2]) *Journ. Ind. Eng. Chemistry* 8 (1916), 78. — [3]) Mc Dermott (see below) designates as "culls" all fruit unsuitable for shipment either through extreme under- or over-size, stem-end rot, traumatic injuries to the peel and blue molds. A few of these culls are disposed of in local markets, others are consumed by cattle or are simply allowed to rot on the ground.

In 1902 a corporation was formed for the production of citrus oil by means of a chemical solvent. The seat of the enterprise was Pasadena and from 1903 to 1907 some 5000 lbs. of lemon oil and about 5300 lbs. of orange oil were produced. During this period the National City plant started work again, but only for a short time.

The Pasadena plant used the peel or skin of the fruit only, while the National City factory used the lemon pulp principally. This was a mistake, for it influenced the success of both undertakings in an unfavourable manner, for a consolidation would have proved a benefit for both sides.

The Pasadena plant finally closed its doors through lack of capital and bad management. It would seem that if this plant had been in the heart of the citrus fruit country and not in Pasadena, to which all the fruit used in the plant was shipped, it should have been a success.

In 1904 a plant of considerable size was laid down in Redlands for the manufacture of orange marmelade. About the same time, in Riverside, a plant for the manufacture of orange wine was built and a large quantity was made and stored in the warehouses, where owing to lack of sale it was allowed to remain until slowly disposed of. The orange wine manufacture never paid because the peel containing the essential oil was discarded, only the pulp being used. Again in Riverside, and at about the same time, a plant was erected for making candied citrus fruit peel and after a short period of operation it closed its doors on account of lack of finances. Various other small plants cropped up in Southern California, but all of them found some considerable drawback in the manufacture of citrus by-products.

The Redlands factory continued to operate in a small way till 1913, although the plant was large enough to handle a considerable volume of fruit. The corporation purchased the Pasadena plant and moved it to Redlands, where they manufactured marmelade as well as essential oil, thus utilizing the whole fruit.

The National City plant was once again re-opened during this period and failed once more, for the fifth time. More recently a plant for manufacturing of citrate of lime and lemon oil was erected in Santa Ana and after a short spell of work it was moved to Riverside where, owing to financial difficulties, it closed its doors.

At the present time there are three plants of considerable size: one at National City, one at Riverside and one at Redlands, with about five other minor plants distributed throughout Southern California.

The question naturally arises why, after fifteen years of continued effort, there is not yet a stable and satisfactory industry for the manufacture of citrus by-products. The author adduces three reasons: 1) the citrus fruit grower has only recently realized the necessity for utilizing his waste fruit; 2) every new industry implies a considerable amount of pioneering work; 3) inefficiency has been the characteristic of all attempts made up to this time to utilize the whole culled fruit, which is the keynote of the matter.

To carry on the manufacture of citrus by-products, five conditions must be considered: 1) the fruit must be cheap and of easy access: 2) the plant must consist of economical and efficient machinery for the production on a large scale, by efficient process; 3) complete utilization of the fruit, so that there will be no waste; 4) conservative business management and ample capital; 5) a stable demand and ready sale for the manufactured products at paying prices.

Chemical control of the factories has been introduced to but a small extent because the promoters of most of the enterprises appeared to consider it superfluous or thought the money could be spent to better advantage for advertisement and other business purposes. To show how desirable it would be for the United States to have a citrus

by-products industry of their own, we refer to the table below, giving the figures of the imports during the fiscal year ending on June 30th. 1913: —

	lbs.	value $
Orange and lemon peel, candied, dry or preserved	654307	34435
Oil of lime	13075	16025
Oil of orange	79797	155199
Oil of lemon	410003	794215
Oil of bergamot	64259	310135
Citrate of lime	5526954	756309
Citric acid	8677	2915
Lemon in brine	1773187	63771
Lemon and lemon peel, candied, dry or preserved	515686	41219
Concentrated lemon, orange or lime juice	—	116572

These imports represent in actual fruit a total of 165000000 lbs. and it is not surprising that efforts should be directed along the lines of utilizing culled fruit in America.

This culled fruit, as it is received, should first be examined and cleaned which is best accomplished by means of brushes in the ordinary fruit-cleaning machine, together with such water as the fruit may require.

Upon the condition of the ripeness of the fruit much depends as to the final product. In the manufacture of lemon oil *f. i.*, a green fruit gives the best oil; any fruit that has been subjected to a sweating process or to slight decay, or ageing, is almost wholly unfit for the manufacture of the finer products.

The next operation to be considered is the peeling of the fruit. The quantity of oil contained in the peel is variable and depends on climatic conditions and other extraneous influences. During the last ten years the quantity of oil in the fruit has decreased, due no doubt to climatic influences and possibly also to certain influences of cultivation and irrigation of the trees.

One of the greatest problems that has confronted the manufacture of citrus by-products, the mechanical separation of the peel from the pulp, may now be looked upon as solved. To peel citrus fruit by hand requires an expenditure of $ 5.— per ton, and this only under the most favourable conditions of labour and fruit. As has been discovered more recently, the peeling of the fruit is not absolutely essential. It has been found sufficient to crush the whole fruit and ground it to a fine pulp from which the essential oil is obtained by extraction, and from the oil-free pulp the juice is separated by centrifugals.

When using the solvent process, the peel is crushed between rollers to a fine paste which contains about 1.9 per cent. of oil in the case of lemons, and 2.2 per cent. with oranges. This paste is mixed with the necessary quantity of solvent which dissolves a portion of the contained oil. It is next run into suitable stills, where the solvent is recovered, the oil remaining behind. This process of extraction may be repeated three times. In this manner a liquid is obtained of a dark reddish colour in the case of oranges or a dark yellowish green colour in the case of lemons.

The composition of orange oil is about as follows: 88.36 per cent. of terpenes, 1.28 per cent. of aldehydes and methylanthranilate and 5.34 per cent. of oleoresins[1]).

[1]) In California the name of "oleoresins" is used quite arbitrarily for the whole oil obtained by extraction as well as for the non-volatile constituents which are supposed to be of particular importance for the flavour of the oil. These constituents are contained in a much smaller percentage in the Italian oils obtained by hand pressing. See also Gildemeister und Hoffmann, *Die ätherischen Öle*, 2nd. ed., vol. III, p. 14.

These "oleoresins" obtained by the solvent process, are interesting bodies, consisting of acid and neutral resins. The acid resins have a rather high melting point and are of wax-like consistency. They have the odour of fresh oranges and they impart to the ripe fruit its characteristic colour.

The neutral resins have a comparatively low melting point; they are inodorous and are separated from the mixture of the two resins by means of properly diluted alcohol, at regulated temperature. By means of ultraviolet rays they may be converted into the aromatic acid resins.

The lemon oil obtained from green fruit contains more citral than that produced from fruit that has been subjected to the sweating process, or is fully ripe.

In the early days it was attempted to obtain the oil from the peel by a powerful hydraulic press, but as the yield only amounted to 2 lbs. of essential oil to the ton of fruit, as against 10 lbs. from the solvent process, this method was soon abandoned. Its failure is explained by the peculiar structure of lemon peel which do not yield their oil readily.

Another method for producing the oil is to grind the peel rather coarsely and place it in tanks capable of agitation, keeping the peel suspended in warm water below the surface. The oil rises to the surface and is skimmed off. The yield, however, appears to be unsatisfactory. This method is practised abroad on a small scale. A similar one will be found described below.

If finely ground peel is subjected to centrifugal action, a larger yield is obtained than by any, except the solvent, process. Under favourable conditions 5 lbs. of oil have been obtained per ton of fruit, in laboratory experiments. This method seems promising, the intermittent feature in charging and discharging of centrifugals being its principal drawback.

Oil produced by the solvent process and properly refined has been kept under proper conditions for five years without any considerable deterioration.

A characteristic of these solvent process oils is their fixing quality. This is evidently due to the high percentage of "oleoresins" which retain the odour after evaporation of the oil; furthermore they appear to prevent oxidation of the terpenes and aldehydes.

The peel is also used for the manufacture of alcoholic extracts and tinctures.

Lemon is perhaps the most widely used flavour in America. It is, therefore, not to be wondered at that 400 000 lbs. of lemon oil are imported annually. In California, unfortunately, the relative planting of oranges to lemons is about five to one.

Now as regards the several by-products, *orange marmelade* takes the first place. In America English marmelade, made from Sevilla oranges, is best introduced. In England the oranges are cleaned, peeled and the seeds removed by a special, highly developed machinery, patented in England. The white pith adhering to the peel, and containing bitter bodies, such as aurantiamarin, is separated from the peel and the peel is then subjected to steaming for a number of hours, in order to soften materially, and to remove part of the essential oil so that the sugar may more readily penetrate and produce a transparent finished product.

The softened peel is then cut by machinery into very fine shreds, the pulp meanwhile has been subjected to a thorough grinding process and is boiled with the required amount of the above mentioned finely cut peel. After some time, and when the proper consistency has been reached, the mass is placed in jars and sealed. The characteristic of English marmelade is its slight bitterness and its tart flavour. The Sevilla oranges do not grow in California and the marmelades made there, which are

in reality jams, have not the characteristic properties of the English article. Sugar being more than twice as dear as in England, Californian marmelade is loaded with fruit pulp. The cleaned fruit are sliced and the slices sometimes subjected to a preliminary soaking in water. They are then boiled with sugar until the required consistency is reached. The orange jam so made has not many characteristics of the English marmelade. It has, however, certain uses, as in the manufacture of biscuits and the like. It differs from the English product in having a sweet taste, and in its jelly-like consistency. Yet, according to Will, it is merely a matter of handling to produce a marmelade very similar to the English article. This could be accomplished by treating the fruit in the same way and by adding some more acid fruit such as grape fruit, or lemon juice from the lemon. The jellying of Californian marmelade is due to the pectin or jellying body which is developed very readily in the orange. Foreign fruit is stripped of the white pith containing the pectin and pectose body, and these consequently do not always enter into the product as an essential characteristic.

In the manufacture of orange paste the whole fruit is ground and boiled with sugar. This product seems to show great promise and is largely used for certain types of biscuits.

Orange juice is produced either by squeezing the whole fruit, separating the oil by known methods or by peeling the fruit and separating the juice from the pulp by presses.

The preservation of orange juice with all its valuable properties of the fresh product is a problem which is not quite solved yet. Possibly the method suggested by J. Takamine yields the most satisfactory results. Of course, it is comparatively easy to clarify an orange juice and bottle and preserve it, but, as Will correctly remarks, such a product is not orange juice in the truest sense, for it has not the colour, flavour or taste of the fresh orange. The juice as it is pressed from the fruits contains certain albuminous bodies, albuminoids in reality, finely divided portions of pulp structure, sugar, acids and mineral salts; density about 1.03. The best and most palatable proportion of sugar and water is about 8 to 1. This proportion of sugar is contained in the fruit only during $2^1/_2$ months of the year, at times only during one month and this short time must be taken advantage of by the manufacturers. The process of preservation is very difficult, for pasteurization and sterilization is very delicate work. Sterilization by ozone has proved disastrous so far and the addition of sugar does not necessarily insure keeping qualities of the juice.

The manufacture of lemon juice is carried on in the same way as the manufacture of orange juice. The juice contains 3.5 to 7 per cent. of acid and from 2 to 10 per cent. of sugar, but sugar and acid content vary with the quality, characteristics and ripeness of the fruit. In efforts to preserve it, the same researches have been made as with orange juice, with more encouraging results except for the fact that lemon juice has in almost all cases turned limey, making it unfit for many purposes.

The process of manufacturing citrate of lime is very simple. The lemon juice is roughly filtered, heated to boiling point and the required quantity of calcium carbonate is then added. After the acid is neutralized or a slight excess of calcium carbonate determined, the insoluble calcium citrate is filtered and dried.

Lemonade syrups are prepared in a simple manner, by mixing the oils with the necessary volume of sugar syrup. An article produced in large quantities is orangeade syrup, but it is a curious thing that its home is not California, but Rochester, N. Y.

Citrus fruit peel, as imported from abroad, is packed in immense hogsheads in brine. To remove the salt, the peel is soaked in water for a certain period and is then placed in a diluted sugar solution, the concentration of which is increased from

day to day. The peel is then dried, after which it is sometimes dipped in a very heavy syrup which, upon final drying, leaves a thick crust of crystallized sugar on the surface. Lemon, orange and citron are the principal fruits used for this purpose.

There are but few acres of citron in California, principally at Riverside; while the production of these groves is prolific, yet attempts to manufacture candied peel have not been altogether successful in competition with candied citron peel from abroad.

As secondary products, really by-products of the by-products, Will mentions a few articles which are not essential to the success of the by-product industry but rather a final refinement of processes, useful in the future development of the industry. Amongst others, it would be possible by isolating the pectin bodies, to prepare a substance capable of serving as a jellifier. Moreover alcohol, as well as vinegar, might be obtained from the fruit. Finally there are three bitter bodies *viz.*, hesperidin, *iso*hesperidin and aurantiamarin which might possibly be put to some technical use.

We may here mention a publication by F. A. McDermott[1]) on the utilization of "culls" from Florida citrus fruits. The by-products to be considered are mainly the juice and the volatile oil, the recovery of citric acid forming one of the minor problems. It was found that by pasteurization alone orange and lime juice could not be preserved; the juice does not keep longer than two weeks, after which time it becomes dark and muddy, a change which is accompanied by a deterioration in flavour which finally becomes offensively acrid. The darkened specimens appeared to be sterile so that the alteration seemed to be due to some chemical action, but though tests were made, these failed to indicate as to what change had taken place. It was found, however, that the removal of the air dissolved in the juice and that in the container above it, followed by pasteurization, was sufficient to prevent deterioration for a considerable time. In fact all failures which occurred within two years could be traced to air having gained access to the juice. As was to be expected, it was also found that it was the oxygen of the air which was responsible for the change, although replacing the air with pure oxygen did not produce as rapid a darkening as might have been expected.

McDermott observed that the most common organized contamination of the orange juice was a strain of the wild yeast ("Kahmhefe"), *Willia anomala,* and it seems that it is this organism which is responsible for the development of the ester odour (apparently ethyl acetate) which may so frequently be noticed in orange juice which has stood for some hours at room temperature. Acetic acid bacteria were also found occasionally. The common blue molds of the peel of the orange, *Penicillium italicum* and *P. olivaceum,* appeared to be unable to grow on the sterilized juice.

The simplest way to remove the air from and above the juice in the containers was to replace it by some non-oxidizing gas; carbon dioxide appeared to be the best. A large number of specimens of orange and grapefruit juices were prepared, in which the juice was charged with carbon dioxide at atmospheric pressure, and the air above the liquid replaced with the dioxide; the content of many of these bottles remained without apparent change for two years or more. Pure nitrogen, hydrogen or methane proved equally satisfactory. Nitrous oxide gave results about like those of pure oxygen. With hydrogen the flavour of the juice seemed to keep best. Carbon dioxide gave a slightly unnatural tang suggesting incipient fermentation.

Sealing in vacuo was also tried and eventually proved to be the most satisfactory method of meeting the difficulty.

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[1]) *Journ. Ind. Eng. Chemistry* 8 (1916), 136.

Grapefruit juice, if not pasteurized, behaved just like orange juice. The behaviour of lemon juice was not closely investigated; it is reported in literature that repeated pasteurization is all that is necessary to prevent deterioration; it was found, however, that this treatment, even on two or three successive days, was insufficient to inhibit a change in orange juice.

Temperature is a very important factor in pasteurization. Temperatures below 60° were insufficient to prevent the development of the spores of *Willia* while, above 70° the flavour began to assume the taste of cooked juice. The best results as far as flavour was concerned, were obtained by pasteurization at 63 to 65° for 15 minutes. Needless to say, sterilization in an autoclave, or at temperatures of 100°, are quite out of the question.

To obtain the best flavour five to ten per cent. of the oranges should be left unpeeled; adding the volatile oil is possible but experiments indicate that this does not give as good a flavour. For grapefruit it was found to be advantageous for the flavour to peel all the fruit and to add from five to ten per cent. of unpeeled oranges; retention of the grapefruit peels produced a liquid of extreme bitterness.

The clarification of the juice is a serious problem. For commercial purposes it is desirable that it should be nearly clear. This is best attained by means of a De Laval clarifier. Chemical clarification with formaldehyde or alcohol is possible though not desirable.

Both orange and grapefruit juices may be evaporated under greatly reduced pressure to a thick syrup and thereupon dried to a brittle, glassy and very hygroscopic solid. It is essential for the retention of a good flavour that the temperature in these evaporation and drying processes should at no time exceed 60°, which condition makes the drying extremely slow. The product so obtained may be dissolved in water and beverages made from the solutions. The flavour of such beverages, however, is not quite up to standard of fresh juice preserved as indicated above, but it is still close to the normal taste of orange juice. Of course, in vacuum treatment the essential oil is lost and it is, therefore, necessary to add some oil for flavouring purposes. Concentrated juice must be carefully pasteurized; this cannot be done in the case of dried juice as it fuses at pasteurizing temperatures, but pasteurization is not necessary, provided water and air are excluded.

The methods practised in Italy in the manufacture of agrumen oils cannot be employed in Florida, hand labour being too expensive. After a number of experiments it was found that a satisfactory oil could be produced by grinding the peel, submitting the ground material to a current of steam at greatly reduced pressure and condensing the oil. From the peel of ordinary Florida oranges 0.5 per cent., from those of Valencia oranges from 1 to 1.5 per cent. of oil was obtained. The liberation of the oil appears to be favoured by previous partial drying of the peel. The oil obtained from Florida oranges as above indicated has been used repeatedly in cakes and candies, in alcoholic solution, and has given excellent results. Another method is to soak the ground peels in water; the oil collects on the surface and is removed. The yield is smaller, but the process less expensive than the previous one. It can, therefore, be made to pay.

The recovery of citric acid from the juice of Florida citrus fruits is hardly worth while, seeing that orange juice rarely contains more than 0.7 per cent., and lime juice rarely more than 1.5 per cent. of citric acid.

As a matter of scientific interest, however, it was found that Wehmer's *Citromyces* molds would grow on the sterilized juice in the presence of calcium carbonate and convert a considerable portion of the residual sugar into citric acid.

Bergamot oil. We have, on repeated occasions, drawn attention to glyceryl ester as an adulterant in bergamot oil[1]). E. Coen[2]) has made similar observations; he describes an adulterant for bergamot oil, which consisted of a mixture of 70 per cent. of triacetin, 20 per cent. of bergamot oil and 10 per cent. of orange oil or terpenes. For the detection of triacetin a modification of the process devised out by our firm[3]) is suggested. 10 cc. of the oil to be tested are treated with 40 cc. of 10 per cent. alcohol, the mixture is reduced to a small volume, neutralized, saponified with alcoholic potash liquor and evaporated to the dry state. The residue is then extracted with a mixture of alcohol and ether and the resultant extract treated with potassium bisulphate; if triacetin was present in the oil under examination, acetic acid will be liberated, along with acrolein vapours. As this publication was at our disposal in the form of a short abstract only we were unable to test this method.

Lemon oil. A sample of lemon oil supplied by a Hamburg firm and submitted to us for analysis from Berlin, was found to have been adulterated in a very ingenious manner. The oil had the following constants: d_{15° 0.8583; α_{D20° + 65°; α_D of the first 10 per cent. of the distillate +63° 10', citral content (phenylhydrazine method) 3.4 per cent.; evaporation residue 2.7 per cent. Generally speaking, all these properties may be looked upon as normal, excepting the rotation which is abnormally high, and the citral content which is comparatively low. But though such deviations may occur in lemon oil, they are rare enough to justify such oils being treated with suspicion. Our suspicion that we had not to deal with a genuine natural product was strengthened by the fact that the evaporation residue showed peculiar properties which induced us to examine it more closely. By re-crystallization from alcohol a fine white crystalline substance was separated which melted at 44°, a closer investigation revealing it to be paraffin. As this body is unknown as a constituent of lemon oil and as in the residue of a guaranteed pure oil, examined for comparison purposes, not a trace of paraffin was to be found, it is evident that the oil under examination was at least considerably adulterated, if it was not altogether an artificial concoction, cleverly adjusted so as to show the correct constants. The adulteration was no doubt the work of a skilled man and serves as a reminder that in chemical analysis even apparently unimportant divergences should not be overlooked.

A sample of terpeneless lemon oil sent us from Vienna also proved to be an adulterated or artificial product. Nothing was to be said as regards its constants, excepting the citral content which, according to the sulphite method, was 81 per cent., which is far too high even for an oil freed from terpenes and sesquiterpenes. The adulteration was proved to certainty after the elimination of the citral, when a predominating odour of geranyl acetate or terpinyl acetate was noticeable, whereas the fatty aldehydes, which are characteristic for terpeneless lemon oil, were conspicuous by their absence.

It would seem that optical rotation of lemon oil is altered but little, or not at all, if the oil is stored in a cool place[4]). During the winter 1907/08 lemon oil samples were collected under the supervision of an officer of the U. S. Department of Agriculture in six different districts of Sicily. Since then these samples had been kept in an ice box in partly-filled, well-stoppered copper vessels. After seven years all the samples

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[1]) See Gildemeister und Hoffmann, *Die ätherischen Öle*, 2nd. ed., vol. III, p. 76. — [2]) *Annali Lab. Chim. Centr. delle Gabelle* **7** (1914), 89; *Annali Chim. Appl.* **3** (1915), 372. From *Journ. Soc. chem. Industry* **34** (1915), 851. — [3]) *Report* October **1910**, 61; April **1911**, 149. — [4]) *Americ. Food. J.; Chem. Abstracts* **10** (1916), 647. From the *Perfum. Record* **7** (1916), 108.

had assumed a turpentine-like odour, but they could still be made use of as inferior lemon oils. The optical rotations in 1906 and 1915 were as follows: 64.92 and 64.92°, 61.53 and 61.63°, 63.33 and 63.16°, 59.58 and 59.58°, 58.30 and 58.06°, 62.22 and 62.01° respectively.

The determination of the volatile esters in lemon oil will be found described on page 90 of this *Report*.

Eucalyptus oil. On page 22 of our *Report* October 1915 we discussed a paper by C. E. Burke and C. C. Scalione on Californian oil of *Eucalyptus Globulus*. In this paper the fact was mentioned that the Australian distillate was in conformity with the requirements of the U. S. Pharmacopœia, but not the Californian oil. P. W. Tompkins[1]) now deals with this fact more closely. He has found that the oil distilled from one year old sucker shoots[2]) of *Eucalyptus Globulus* differs very considerably from the oil obtained from leaves of older trees, as will be clear from the following table: —

Oils of *Eucalyptus Globulus*.

	Age of the trees		
	1 year	5 years	30 years
Yield	0.09 p.c.	0.21 p.c.	0.84 p.c.
d_{250}	0.890	0.906	0.908
Solubility in 70 p.c. alcohol	insoluble	45 vol.	15 vol.

The abnormal properties observed occasionally in Californian oils are probably due to young leaves having been used for distillation. But even the oil from normal leaves of old trees shows an unsatisfactory solubility, as compared with U. S. P. requirement, which is a solubility of 1 vol. of oil in 3 vol. of 70 per cent. alcohol, such as is possessed by Australian oils. Tompkins has now examined an authentic oil of *Eucalyptus Globulus* obtained from Australia and has found that even this oil is soluble only in 8 vol. of 70 per cent. alcohol. d_{250} 0.9123; $[\alpha]_{D250}$ + 3.9°; cineole content 54 per cent. (phosphoric acid method), whereas Californian oils of *Eucalyptus Globulus* showed the following average properties: d_{250} 0.906; $[\alpha]_{D250}$ + 8.0°; soluble in 15 vol. of 70 per cent. alcohol, cineole content 52 per cent. (phosphoric acid method). The author explains the difference in solubility of Californian and Australian oils of *Eucalyptus Globulus* by the fact that the Australian oil of commerce is derived in reality from other species, for, as Baker informed him by letter, the oil is rarely obtained from *Eucalyptus Globulus* in Australia, other kinds being distilled which yield oils richer in cineole, such as *f. i. Eucalyptus polybractea*.

From this it would appear that, as a matter of fact, oil of *Eucalyptus Globulus* does not dissolve readily. It would be possible to bring the Californian oil up to the U. S. P. solubility standard by means of rectification, but this would entail a loss of about 15 per cent. of oil. In Tompkins' opinion it would be better if U. S. P. were to stipulate a solubility of 1 vol. in 18 vol. of 70 per cent. alcohol; in that case the normal Californian Globulus oils would be covered by the requirements of the Pharmacopœia.

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[1]) *Journ. Ind. Eng. Chemistry* 7 (1915), 995. — [2]) As will be known, the young foliage of most kinds of Eucalypti is differently formed from that of older branches. Wherever new shoots grow from tree stumps, only sucker leaves are produced which are frequently used for distillation in California.

At the same time a cineole content of 60 per cent. (resorcinol method) or 50 per cent. (phosphoric acid method) should be insisted upon.

It seems to us that the indifferent solubility of *Eucalyptus Globulus* oils is a characteristic peculiar to Californian oils, for in the course of more than 30 years we ourselves have examined a large number of Globulus oils of Australian, French, Spanish, and Algerian origin, the raw material for which had consisted exclusively of the leaves of *Eucalyptus Globulus*. Nevertheless we found, almost without exception, that the oils were soluble in 2 to 3 vol. and more of 70 per cent. alcohol; only in a few isolated cases up to 7 vol. of the solvent were necessary. Even the above-mentioned communication by Baker to Tompkins does not alter the case, for nothing is said about solubility, only the cineole content being mentioned which, however, is not at all greater in oil of *Eucalyptus polybractea* than with Globulus oils, for in their exhaustive monograph on Eucalyptus oils[1]) Baker and Smith state that a distillate produced by themselves from the leaves of *Eucalyptus polybractea* contained 57 per cent. of cineole, which is not an extravagantly large percentage. The solubility of this oil was exactly the same as with a Globulus oil obtained by the same workers themselves (monograph, page 96). It follows that in his argument Tompkins can hardly base himself on the testimony of Baker. It is not improbable that the indifferent solubility of the Californian oils is due to the particular method of distillation.

According to H. G. Smith[2]) butyl butyrate belongs to the list of constituents of a certain class of eucalyptus oils, although in most cases it occurs in very small amount. The ester is possibly formed from two molecules of butaldehyde which occurs in most eucalyptus oils and is responsible for the unpleasant odour noticeable in crude oils. *n*-Butyric acid has been identified in many eucalyptus oils, the acid is probably derived from the hydrolysis of the ester, because a corresponding change does take place when oil of *Eucalyptus Perriniana*[3]) has been stored a long time. The abnormally low refractive index (1.4538) of the low-boiling fractions led to the detection of the ester. The saponification number of the crude oil was 52.6, representing 13.52 per cent. of an ester having a molecular weight of 144. The saponification number of the fraction distilling below 190° (75 per cent. of the oil) was 57.2, representing 14.7 per cent. of the esters in this fraction. Thus the greater proportion of the total esters in the oil of *E. Perriniana* consists of butyl butyrate.

The manner in which this ester was identified is not given in the paragraph mentioned.

Another constituent of some eucalyptus oil is a phenol, hitherto unknown, which Smith[4]) calls tasmanol, because it occurs in the oils of some species of eucalyptus *(f. i. E. linearis* and *E. Risdoni)*[5]) which are considered endemic in Tasmania. The phenol was recovered from the crude oil by shaking with aqueous solution of sodium hydrate, washing the aqueous solution with ether and acidifying and extracting with ether. The residue, which contained small amounts of acetic and butyric acids, was washed with sodium carbonate solution and the phenol distilled. B.p. 268 to 273° (not corrected); $d_{23°}$ 1.077; $\alpha_D \pm 0°$; $n_{D22°}$ 1.5269. Besides being soluble in alkalies, the phenol is soluble in ammonia and partly soluble in sodium carbonate solution, but not in sodium bicarbonate. The reaction with ferric chloride in alcoholic solution is characteristic,

[1]) A research on the eucalypts, especially in regard to their essential oils. Sydney 1902. — [2]) *Journ. Royal Soc. of N. S. W.* **48** (1914), 464; *Perfum. Record* **6** (1915), 347. — *Journ. Chem. Soc.* **108** (1915), I. 978. — [3]) See *Report* October **1913**, 57. — [4]) *Journ. Royal Soc. of N. S. W.* **48** (1914), 518; *Perfum. Record* **6** (1915), 347. — *Journ. Chem. Soc.* **108** (1915), I. 978. — [5]) See *Report* Oktober **1913**, 57.

the deep red colour remaining permanent for several days after the alcohol had evaporated. It contains one methoxy-group and appears to have two phenol groups in the para-position. Tasmanol appears to occur in the cineole-phellandrene oils, but in the oils which do not contain phellandrene another phenol occurs which, although probably allied with the other, is not identical and may perhaps represent a new substance. This phenol gives a green colour with ferric chloride and is readily soluble in sodium carbonate solution, but not in sodium bicarbonate.

In another place Smith[1]) deals with the question of using *Eucalyptus Smithii* R. T. B.[2]) for cultivation purposes; the leaves yielded an excellent oil; the wood, however, was of little value. The best way is to cultivate "suckers"[3]) which develop a plentiful supply of foliage and are easily collected. The oil has the following properties: d 0.9098 to 0.9210; α_D +4.2 to +9.2°; sap. v. 1.3 to 5.6. It dissolves in 1 to 2 vol. of 70 per cent. alcohol and contains from 61.5 to 85.3 per cent. of cineole. Further constituents are pinene, a phenol, eudesmol (m. p. 79°), a paraffin melting at 64°, and a small amount of esters and sesquiterpenes.

The method elaborated by J. L. Turner and R. C. Holmes for the determination of cineole by means of arsenic acid, which we discussed on page 19 of our last *Report* in reference to a paragraph printed in the *Perfumery and Essential Oil Record* [6 (1915), 20] has since then been reported upon in another journal[4]) in a more exhaustive manner.

Göppert[5]) reports about two cases of bronchorrhœa and blennorrhœa which were successfully treated by inhalation of eucalyptus oil, the cure being effected in from 5 to 14 days. In one case there was a relapse after a few weeks, without there being, however, an excess of secretion. It is recommended to inhale eucalyptus oil by means of a mask, made from a paper bag. Inhalation should take place about three or four times a day, for about ten minutes every time, with repeated interruptions. Moreover eucalyptus oil should be sprinkled on the pillow at night, and on the handkerchief during the day, so as to enable the patient to inhale constantly.

Oil of Evodia rutæcarpa. From the volatile oil of the fruits of *Evodia rutæcarpa*, Hook. et Thoms. (N. O. *Rutaceæ*) Asahina and Kashiwuki[6]) isolated a terpene differing from the terpenes known so far, and which they called evodene. On being reduced with platinum black dimethyloctane was obtained, proving its relation with myrcene. It forms a dihydro product, the tetrabromide of which remains liquid, whereas the tetrabromide of dihydromyrcene melts at 88°. Evodene boils at 67° (20 mm.); d 0.799; n 1.4843.

From the fruits the authors furthermore isolated a crystalline substance melting at 278°, the evodiamine, which, on being heated with alcoholic potash liquor, is split into a base $C_{11}H_{10}N_2$ and methylanthranilic acid.

The designation evodene of the new terpene is inadmissible inasmuch as Semmler and Schossberger[7]) called a new terpene, isolated from the oil of *Xanthoxylum (Evodia) Aubertia* in 1911, by this name (evodene).

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[1]) *Journ. Royal Soc. of N. S. W.* **49** (1915), 158; *Journ. Chem. Soc.* **110** (1916), I. 272. — *Perfum. Record* **7** (1916), 83. — [2]) See Gildemeister und Hoffmann, *Die ätherischen Öle*, 2nd. ed., vol. III, p. 269. — [3]) Suckers are shoots which grow from the tree trunks, bearing young foliage. — [4]) *Americ. Journ. Pharm.* **87** (1915), 101. — [5]) *Therap. Monatsh.* **29** (1915), 514. — [6]) *Journ. Pharm. Soc. of Japan; Pharm. Weekblad* **1916**, 181. From *Apotheker Ztg.* **31** (1916), 115, and *Perfum. Record* **7** (1916), 13. — [7]) *Berl. Berichte* **44** (1911), 2885; *Report* April **1912**, 134.

Oil of Galbanum. P. H. Marsden[1]) has examined a species of galbanum originating from Basrah on the Persian Gulf. The drug was enclosed in what at first appeared to be a hollow umbelliferous stem. The odour was normal, with a faint suggestion of turpentine. The inner part of the sample consisted of a sticky mass, the outer layers being formed of yellow tears of 0.5 to 1 cm. diameter; débris was seen only on the outside. The taste was persistently bitter. The drug contained 7.36 per cent. of moisture and 2.29 per cent. of ash. Two mericarps were picked out of the gum-resin which were examined microscopically, but it was not found possible to establish the botanical source of the drug in this manner although it may be looked upon as probable that the mother-plant is a species of *Ferula.*

As will be known, three *Ferula* species are given as mother-plants of the galbanum of commerce, *viz., F. galbaniflua,* Boissier, *F. rubricaulis,* Boissier and possibly also *F. Schair,* Borzczow[2]).

Oil of Geranium. In 1914 the export of geranium oil from Réunion amounted to 70000 ko. as against 43000 ko. in 1913. The price rose from fr. 40.— to fr. 77.50 in August 1914, but since the outbreak of the war it receded to fr. 25.— and even fr. 20.— per ko., which induced the planters to restrict production very considerably[3]).

Oil of Ginger. In the course of an examination of a ginger oil which had been freed from terpenes and sesquiterpenes, B. T. Brooks[4]) found, besides citral, methylheptenone, nonaldehyde, linalool, *d*-borneol, acetates, caprylates and a phenol (possibly chavicol), a sesquiterpene alcohol $C_{15}H_{26}O$, which imparts the characteristic mild odour to ginger oil and to which he gave the name of *zingiberol.* From 150 gr. of ginger oil freed from terpenes and sesquiterpenes he isolated 24 gr. of zingiberol of a boiling point of 154 to 157° (14.5 mm.). When heated, this alcohol splits off water and forms a hydrocarbon $C_{15}H_{24}$ of the boiling point 255 to 257°, the zingiberene or *iso*zingiberene from which *iso*zingiberene hydrochloride (m. p. 169°) results when treated with hydrochloric acid gas in glacial acetic acid solution. Zingiberol, when treated with gaseous hydrogen chloride or gaseous hydrogen bromide yielded *iso*zingiberene dihydrochloride (m. p. 169°) and *iso*zingiberene dihydrobromide (m. p. 176°) respectively.

Oil of Gingergrass. A peculiar kind of gingergrass oil was offered to us recently from Hamburg. To the expert the oil revealed itself as a barefaced sophistication by its odour, for it really smelled like a turpentine oil perfumed with gingergrass oil and we merely mention it here to show that even now, when turpentine oil is conspicuous by its absence, it must still be looked for as an adulterant. The constants were of course in keeping with the odour, specific gravity was too low, acetylation value was much too low and solubility was quite indifferent: $d_{15°}$ 0.8927; α_D +11°7'; acid v. 5.4; ester v. 12.1; after acetylation 63.5; it only dissolved in about 5 vol. of 90 per cent. alcohol and did not yield a clear solution even with 10 vol. of 80 per cent. alcohol. Pure gingergrass oil has a specific gravity of 0.90 to 0.953 at 15°, an acetylation value of 120 to 200 and dissolves in most cases in 2 to 3 vol. of 70 per cent. alcohol, and invariably in 0.5 to 1.5 vol. of 80 per cent. alcohol.

It was not to be wondered at that the boiling point was in keeping with the other constants, nearly half the oil distilling at the boiling point of turpentine oil, *viz.,* 155

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[1]) *Pharmaceutical Journ.* **95** (1915), 356. — [2]) See Gildemeister und Hoffmann, *Die ätherischen Öle,* 2nd ed., vol. III, p. 395. — [3]) *Chem. Ztg.* **40** (1916), 18. — [4]) *Journ. Americ. Chem. Soc.* **38** (1916), 430.

to 165°, whereas true gingergrass oil has a higher boiling point. The fraction consisted chiefly of α-pinene which was identified by its nitrolbenzylamine, m. p. 123°. As pinene does not belong to the constituents of gingergrass oil, the proof of its presence is also the chemical proof for the addition of turpentine oil.

Oil of Formosan Hinoki wood. The Hinoki tree *(Chamœcyparis obtusata,* S. et Z., N. O. *Pinaceæ)* is largely cultivated in Japan and supplies a valuable timber; in the mountainous regions of Formosa it forms extensive virgin forests. From the wood So Uchida[1]) obtained 2.4 per cent. of an oil which in the crude state formed a reddish-brown, readily-mobile liquid possessing an empyreumatic odour. After rectification and treatment with dilute sodium carbonate solution it showed a density of $d_{15.5°}$ 0.8821; $[\alpha]_D$ + 50.37° (10 per cent. solution in chloroform); $n_{D18.5°}$ 1.4990. About 70 per cent. of the oil consisted of *d*-α-pinene which was characterized by its hydrochloride and purified by its sublimation; m. p. 132.5 to 133.5°. The figures occurring in literature, *viz.,* 125° (Wallach) and 131° (Long) Uchida considers incorrect. The oil also contains about 24 per cent. of sesquiterpenes, of which cadinene was proved by the hydrochloride (m. p. 117 to 118°). The hydrobromide melted at 124 to 125°.

Oil of Juniper. According to a communication published in the *Seifensieder-Zeitung*[2]) the farmers inhabiting the mountain districts of Norway, such as *f. i.* the Anorsätzene, 1½ miles from the station Myre, Gudbrandsdalen, carry on as a side-line the manufacture of juniper oil, ("Ener-Olie") for which they receive Kr. 2.15 for a bottle of about ¾ litres capacity in the chemist's shops. Apart from medicinal purposes the oil is also used in some places for the production of a beer-like beverage as well as for gin. The distillation of the young shoots is carried out in a primitive way in two vats which are connected by two tubes. One of these vats, with perforated bottom, is filled with the juniper shoots and placed on a vessel containing boiling water, the other vat, filled with cold water, acts as condenser.

As will be evident from this description, there can here be no question of the normal juniper oil, distilled from berries, but of a kind of juniper needle oil. No indications are given as regards the properties of the oil.

Oil from the wood of Juniperus oxycedrus[3]). For the distillation the same parts of the shrub were taken which ordinarily serve for the preparation of oil of cade, *i. e.,* the lower parts of the stems, peeled but still covered by the bast (inner bark). After the wood had been comminuted, it was distilled in water over the naked fire (the condensed water being returned to the still), and also without water by passing a current of steam.

The properties of the resulting, viscid, yellowish oil were: $d_{15°}$ 0.925 to 0.927; α_D — 31.42°; boiling temperature between 260 and 300° (ordinary pressure), 73 per cent. of the oil distilled between 260 and 280°; it is soluble with slight turbidity in equal volumes of turpentine oil, light petroleum, or carbon disulphide, in twelve times its volume of ethyl alcohol, and in twenty times its volume of methyl alcohol.

The oil content was 3.0, 2.67, and 1.8 per cent. respectively. These three figures are for the same wood, but the first two yields refer to water distillation, the last one to distillation by steam. It goes without saying that both kinds of distillation should

[1]) *Journ. Americ. Chem. Soc.* **38** (1916), 699. — [2]) *Seifensieder Ztg.* **42** (1915), 785. — [3]) R. Huerre, *Journ. de Pharm. et Chim.* VII. **12** (1915), 273.

yield the same amounts of oil, the differences, however, are explained by a remark of the author. It appears that when distilling with water, the oil obtained was weighed every time the distillation water was returned to the still, and once, before the conclusion of the distillation, the wood was left lying in the water in the still for eight days, subsequent distillation yielding three times the quantity of oil of the previous distillation. This is a sure sign of diffusional distillation, as von Rechenberg[1]) has called and explained it. Only the readily accessible volatile oil can volatilize and be carried away by the steam, whereas the oil enclosed in the untouched cells can only penetrate through the walls of the cells by slow diffusion. This process requires the more time, the coarser the pieces of the raw material. The consequence is incomplete and uneven distillation results. The term used by the author as to sufficient comminution is not, therefore, applicable, for comminution must have been insufficient. For this reason the question raised by the author, as to whether wood gathered in autumn or in spring contains more oil, cannot be answered definitely. On the other hand, he established beyond doubt that the content of volatile oil decreases very considerably with storing the wood, for juniper wood which had been kept in a bag for about a year only yielded 0.275 per cent. of volatile oil.

Finally the author examined as to whether rectification of the oil had best be carried out by water distillation, or distillation with superheated steam under atmospheric pressure, or under reduced pressure. He found that with the last-named method the ratio of oil to water in the distillate was most favourable.

His findings are correct, as they are based on scientifically recognized facts. Evidently the author has remained ignorant of the research work done by von Rechenberg[2]) who not only explained the processes observed in the distillation by superheated steam but also determined them quantitatively.

Oil of Lemongrass. Some years ago E. J. Parry[3]) observed that West Indian as well as Cochin lemongrass oils showed a gradual decrease in citral content when stored. This decrease was up to 5 per cent. with West Indian oil after several years of storage, with Cochin oils it was observable even after two months. At the same time solubility decreased likewise.

When reporting on Parry's publication[4]) we expressed our surprise at the fact that in no case had the drop in citral value been more than 5 per cent., and had ventured the opinion that the products formed in the process of alteration might possibly have a preserving effect on the remaining citral. We ourselves had observed no change either in citral content nor in solubility in a lemongrass oil from Barbados, even after two years' storing.

That the drop in citral value may, however, be far more considerable than 5 per cent. is now shown by observations[5]) made on this subject. At the same time the alterations were determined which the specific gravity of lemongrass oil underwent during storage. In a Bourbon oil which had a specific gravity of 0.889 and a citral content of 78 per cent. in July 1913 the specific gravity was found to have risen to 0.895 and the citral value to have decreased to 60 per cent. in April 1916, *i. e.* after nearly 3 years. The drop in citral value was, therefore, 18 per cent.

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[1]) C. v. Rechenberg, *Theorie der Gewinnung und Trennung der ätherischen Öle durch Destillation.* Miltitz near Leipzig 1910. p. 418. — [2]) von Rechenberg and Weißwange, *Journ. f. prakt. Chem.* II. **72** (1905), 478. — von Rechenberg, *Theorie* etc. *l. c.*, page 403. — *Report* October **1905**, 78. — [3]) *Perfum. Record* **4** (1913), 40. — [4]) *Report* April **1913**, 70. — [5]) *Perfum. Record* **7** (1916), 95.

An oil from the same shipment taken from a container which had not been opened before showed the following properties in April 1916: d 0.892; citral value 68 per cent. Two samples of cochin oil showed the following alterations after storage: —

	October 1912	April 1913	April 1916 N° I	April 1916 N° II
d	0.898	0.899	0.925	0.923
citral . . .	78 per cent.	74 per cent.	64 per cent.	60 per cent.

At an earlier date J. C. Umney and S. W. Bunker[1]) had observed that the citral content of a "wet" lemongrass oil had dropped from 79 to 68 per cent. already after three months, whereas a second sample which had been carefully "dried", other conditions being equal, showed a considerably smaller decrease, *viz.*, from 79 to 74 per cent. The conclusion is that lemongrass oil should not only be protected from light and air, but should also be in a perfectly "dry" condition before being stored.

Oil of Libocedrus decurrens[2]). The volatile oil contained in the needles, twigs and bark of the Californian conifer *Libocedrus decurrens*, Torrey (incense cedar) has been examined by A. W. Schorger[3]). In order to determine the influence of storage on the yield of oil fresh needles were distilled, as well as needles which had been kept in the open air for some weeks. The yield from fresh needles was from 0.206 to 0.226 per cent., from stored needles from 0.240 to 0.267 per cent. (calculated on the weight of the fresh material). It was also found that the needles are richer in oil during the months of May and November than in June and October, while the total borneol content was greatest during August and September. Trees grown in open spaces furnished a material richer in oil than those surrounded by other timber.

In order to determine the properties of the oil at different stages of the distillation, the distillate from one run of ten hours' duration was collected in four fractions.

About 89 per cent. of the oil passed over during the first four hours, the oil having normal properties, the remainder showing abnormal constants.

With oil from twigs and needles, obtained to the extent of 0.166 to 0.300 per cent., Schorger established the following figures: $d_{15°}$ 0.8665 to 0.8739; $\alpha_{D20°}$ —3.20 to +38.68°; $n_{D15°}$ 1.4754 to 1.4775; acid v. 0.48 to 1.30; ester v. 18.49 to 24.27; after acet. 28.64 to 39.83. The majority of the oils were pale, greenish yellow in colour, though some samples were dark greenish brown.

In an aqueous extract of the first fraction furfural was detected by means of the colour reaction with aniline and hydrochloric acid. The oil contained 12 to 16 per cent. *l*-α-pinene (characterized by the nitrolpiperidine, m.p. 117 to 118°), *d*-sylvestrene (dihydrochloride, m. p. 72 to 72.5°), *d*-limonene (tetrabromide, m.p. 113°) and dipentene (tetrabromide, m. p. 124 to 124.5°). The total sylvestrene, limonene, and dipentene content amounted to 54 to 58 per cent. The oil also contained 8 per cent. bornyl acetate, determined by saponification to borneol (oxidation to camphor) and acetic acid (analysis of the silver salt), as well as 4 per cent. of free borneol. In the highest-boiling portions of the oil 6 to 7 per cent. of a sesquiterpene was found which the author failed to identify with any of the known sesquiterpenes. He called it tentatively: *libocedrene*. B. p. 260 to 280°; $d_{20°}$ 0.9292; α_D +6.4°; $n_{D20°}$ 1.4994. The hydrochloride melts at 132 to 133°.

From the bark of *Libocedrus decurrens* 0.14 per cent. of a faint greenish yellow oil were obtained: $d_{15°}$ 0,8621; $\alpha_{D20°}$ +1.10°; $n_{D15°}$ 1.4716; acid. v. 0.60; ester v. 3.22;

[1]) *Perfum. Record* 4 (1913), 38. — [2]) See *Report* April **1915**, 52. — [3]) *Journ. Ind. Eng. Chem.* 8 (1916), 22.

after acet. 9.53. It contained large quantities (75 to 85 per cent.) of *l*-α-pinene (nitrolpiperidine, m. p. 117 to 118°), 5 to 6 per cent. dipentene (dihydrochloride, m. p. 48 to 49°), as well as, presumably, small quantities of borneol, *i. e.* bornyl acetate and high-boiling constituents of a greenish colour.

Oil of Limes. The exports of lime oil from Dominica[1]) during the years 1892 to 1914 are illustrated by the following table: —

	Gall.	£		Gall.	£		Gall.	£
1892 . . .	1127	87	1900 . . .	4446	4104	1908 . . .	4860	4659
1893 . . .	1346	1877	1901 . . .	3907	2866	1909 . . .	5403	5239
1894 . . .	1469	1051	1902 . . .	5709	3207	1910 . . .	6780	5875
1895 . . .	1561	1762	1903 . . .	3050	1493	1911 . . .	6364	5401
1896 . . .	1942	3364	1904 . . .	2804	860	1912 . . .	5207	4834
1897 . . .	2884	4713	1905 . . .	4163	1947	1913 . . .	6875	9833
1898 . . .	3560	4432	1906 . . .	4706	3016	1914 . . .	5603	10138
1899 . . .	3587	4492	1907 . . .	4675	4133			

The great hurricane which struck Montserrat in 1899 contributed very considerably to the progress in Dominica. It appears that many Montserrat labourers and their families sought refuge in Dominica and as they knew the work of the lime industry they helped to develop the increased output. The retrogression of the years 1903 and 1904 was caused by great drought and insect pests.

Besides the fine hand-pressed lime oil above figures also include the inferior distilled oil which is used in the United States in fairly considerable quantities.

Oil of Linaloe. Two samples of linaloe oil sent to the editor of the *Perfumery and Essential Oil Record* in London[2]) from Mexico differed very considerably in odour and other properties from normal oils and resembled mixtures of lavender and petitgrain oils rather than Mexican linaloe oil. The constants were as under: —

$d_{15°}$	0.897	0.893
α_D	— 2° 30′	— 2° 30′
$n_{D20°}$	1.4600	1.4610
ester (linalyl acetate) .	52.4 per cent.	48.7 per cent.
total linalool	54.8 „ „	57.6 „ „

The high ester content is of particular interest, the linalool percentage being comparatively low. In order to be able to investigate the botanical origin, samples of the wood and blossoms have been asked for.

We ourselves had occasion, some years ago, to report on Mexican linaloe oils of an unusually high ester content[3]), but the amount of linalyl acetate was only up to 26 per cent. (ester v. 75), the oils otherwise being of a completely normal quality.

Oil of Massoi bark. According to a paper by C. Griebel and A. Freymuth[4]) the so-called massoi-bark, which had been imported from German New Guinea at the time, has of late been successfully worked up into soup condiments, &c. Nothing definite

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[1]) *Perfum. Record* 7 (1916), 210. — [2]) *Perfum. Record* 7 (1916), 62. — [3]) *Report* October **1912**, 80. — [4]) *Zeitschr. Untersuch. d. Nahrungs- u. Genussm.* **31** (1916), 314.

could be ascertained regarding the botanical origin of this bark which, in the authors' opinion, is identical with the bark distilled by us some years ago[1]).

The anatomical results which are clearly described and illustrated show that we have undoubtedly to deal with a lauracea, most likely a species of *Cinnamomum,* as the mother-plant. The bark consisted of pieces about 4 inches long, 1 1/2 to 3 1/4 inches wide and from 2 to 4 (average about 3 1/2) inches thick, but slightly curved. On the outside the bark was covered in part by a silver-grey or brownish-grey cork-like cracked coating. This coating is, however, in most cases severed along with parts of the primary cortex, the colour of the outside appearing reddish-brown, the inner side showing cinnamon coloration. The fracture of the bark shews short fibre, the inner part of the secondary cortex being scaly in parts. The odour distinctly reminds of eugenol as well as safrole with a tang resembling nutmeg. The safrole odour is most pronounced when the bark is fractured or powdered. The taste is strongly acrid like eugenol.

The microscopical examination of samples of the bark of *Massoia aromatica,* Becc. from the collection of the Royal Botanical Museum in Dahlem revealed this material to be mixed. Two samples originating from Java, which closely corresponded with the description of *Massoia aromatica,* possessed an anatomical structure differing very considerably from the massoi bark examined by the authors. A third sample proved to be absolutely identical with the bark under examination. This sample bore the description of *Massoia aromatica,* as well as a fourth one, which, however, was completely different from the two other samples, though it also came from a lauracea, possibly a *Cinnamomum* species. According to the indications on the label the two last-named samples originated from New Guinea, which shows that the natives bring to market as "Massoi" different kinds of bark.

Massoia aromatica, Becc. differs from the bark examined by Griebel and Freymuth *inter alias* in the structure of the secondary cortex which shows numerous, large and isolated stone-cell groups, even in the inner parts. The center of these stone-cells is usually filled by one or two large oxalate crystals.

Another characteristic sign is found in the slight but evenly-thickened bast fibres, the walls of which are permeated by fairly numerous diagonal pore-fissures. On the cross-section the fibres appear almost round and they are conspicuous by their great lumen. *Massoia aromatica* cannot, therefore, be looked upon as mother-plant of the drug examined by the authors.

In order to determine the properties of the oil contained in the bark, 300 gr. powdered bark were distilled in a current of steam, when 7.66 and 8.17 per cent. of oil were obtained. This oil was a pale yellow liquid smelling principally of eugenol. d_{15° 1.038; n_D 1.5405. Upon the addition of ferric chloride in alcoholic solution, a bluish green coloration took place. When tested for eugenol 81.1 per cent. of phenols were found. The eugenol, when isolated, boiled at 244°. The non-phenols (safrole and terpenes) were shaken with permanganate solution when piperonal was formed amongst other substances.

At the time, we had obtained from New Guinea massoi bark 6 to 8 per cent. of an oil shewing a density of 1.04 to 1.065 and containing 70 to 75 per cent. of eugenol and safrole. As will be seen the oil obtained by Griebel and Freymuth shews great similarity with our distillate which leads to the conclusion that the distillation material was identical.

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[1]) Gildemeister and Hoffmann, *The Volatile Oils,* 2nd. ed., vol. II, p. 489.

Oil of Monodora Myristica[1]). In the Imperial Institute in London[2]) two parcels of seeds of *Monodora Myristica*, Dun. (N. O. *Anonaceæ*) were subjected to distillation. These seeds are called "Owere seeds" on the Gold Coast. The first parcel (I) consisted of material of good appearance, the yield being 5.9 per cent. From the second parcel (II) only 2.2 per cent. of oil were obtained, which may possibly be due to the indifferent state of the material. The properties of the two oils were as follows: —

	$d_{15°}$	α_D	acid v.	ester v.	ester v. after acet.	solubility in 90 per cent. alcohol
I	0.849	— 44° 40′ (20°)	1.2	1.9	52.9	6 vol. and more
II	0.8592	— 57.8° (25°)	1.4	6.4	35.5	4.5 vol. and more

The Imperial Institute has made enquiries with some firms as to the practical value of the oil, but it appears that it is almost worthless for industrial purposes.

Oil of Mustard seed. In a paper by C. A. Huber and P. van der Wielen[3]) on expressed oil of mustard seed and the composition of black mustard seed we find a few notes on the percentage of volatile oil in black mustard seed of different origin. The determination was carried out after the maceration process, as described in the German Pharmacopœia V. The following figures were found: —

Origin	Percentage of fat	of volatile oil
Holland	25.7 per cent.	1.23 per cent.
North Holland	28 „ „	1.15 „ „
England	31.4 „ „	1.07 „ „
Russia	37.01 „ „	0.63 „ „
Caucasia	29.8 „ „	1.07 „ „
Italy	32.5 „ „	0.87 „ „
Sicily	32.9 „ „	0.94 „ „
Roumania	35.7 „ „	0.66 „ „
Bombay	33.5 „ „	1.07 „ „

D. E. Tsakalotos[4]) has found from 1.13 to 1.21, average 1.17 per cent. of volatile oil in the seeds of black mustard *(Brassica nigra*, Koch, N. O. *Cruciferæ)* cultivated in Greece. It consisted chiefly of allyl mustard oil. Boiling point 149 to 152° at 763 mm.; $d_{11°}$ 1.019; $\alpha_D \pm 0$; $n_{D11°}$ 1.537.

Oil of Neroli. Although this year's blossoming season of the orange trees exceeded expectations in France, the result, owing to a variety of unfavourable conditions, was anything but satisfactory[5]). After a prolonged rainy season the blossoms developed with unusual rapidity during the first few sunny days so that the few work-people that had come across from Italy this year were overwhelmed with work. The blossoms had to be gathered even before they had fully opened, which had an unfavourable influence on the yield.

In Golf-Juan Vallauris, the seat of the "Société coopérative de production des propriétaires d'orangers des Alpes-Maritimes" there was lack of water owing to a defect in the supply-plant. In consideration of all these circumstances the price for the orange blossoms was fixed at 65 centimes per kilo.

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[1]) See Gildemeister and Hoffmann, *The Volatile Oils*, 2nd. ed., vol. II, p. 407. — [2]) *Bull. Imp. Inst.* **13** (1915), 346. — [3]) *Pharm. Weekblad* **52** (1915), 1410. From a reprint kindly sent us. — [4]) *Journ. de Pharm. et Chim.* VII. **13** (1916), 78; *Chem. Zentralbl.* **1916**, II. 19. — [5]) *Parfum. moderne* **9** (1916), 50.

In Morocco orange blossoms are distilled by the natives in Marakesh and Fez[1]). About 80 per cent. of the oranges cultivated in the neighbourhood of Fez belong to the variety of *Citrus bigaradia*. In the district of Marakesh harvesting of the blossoms terminates in April while around Rabat it only reaches its height in that month and in Mekines it ends even later. In Fez the gathering of the blossoms lasts about twenty days. Marakesh and Fez are without doubt the most important centres of distillation. The natives possess only very primitive apparatus, and they produce orange flower water, but not the oil.

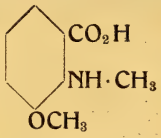
In a previous *Report* we had dealt with the changes which take place in medicinal waters, and the means of sterilising such preparations[2]). In this connection we would refer to a paper by R. Guyot[3]) on the green coloration of orange flower water and other distilled waters and solutions. The coloration is due to an aerobic microbe forming colourless clusters of rod-like organisms, 4 to 5 μ long and 0.5 μ wide, which are colored by basic aniline dyes and methyl blue and assume the Ziehl and Gram colorations. This microbe is different from *Bacillus liquefaciens fluorescens* and from most water bacteria producing green fluorescence. It produces a green, non-fluorescent coloration. It also differs from *Bacillus pyocyaneus* as well as from Lesage's bacillus. The new microbe appears to be able to exist without giving off the green colour; its colour-forming properties are dependent upon extraneous surroundings and the composition of its cultivating solution. Oxidating media and oxygen favour the development of the green coloration while reducing substances weaken it and make it disappear entirely. Light has a favourable influence on the development of the green colour. Zinc acts as a reducing substance; this is the reason why green coloration does not take place with orange flower water stored in zinc vessels. An alkaline reaction of the liquid favours the development of the microbe.

The green colouring matter evidently belongs to the group of aurantiachlorines; it is insoluble in alcohol, methyl alcohol, ether, chloroform, and benzene, but dissolves in water. To isolate the colour, undyed wool is immersed in the liquid when the colour is precipitated on the wool. If the wool is treated with diluted acids the green colour is converted into a brick-red one, soluble in alcohol, methyl alcohol, ether, chloroform, and benzene. If this solution is neutralized, the red colour is once again converted into the green colour, soluble in water. Cherry laurel water never shows green coloration. No decrease in odour is noticeable in the waters owing to the change involved by the green coloration; on the contrary, with orange flower water for instance the opposite effect may be observed.

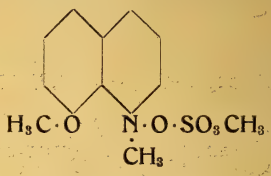
Oil of Nigella. A few years ago[4]) we reported on a synthesis of damascenine, the alkaloid of the oil of *Nigella damascena*, L., carried out by J. Ewins, by which synthesis the formula established by us for the alkaloid at an earlier date[5]), $C_{10}H_{13}O_3N$ was confirmed. In damascenine Ewins recognized the methyl ester of 2-methylamino-3-methoxybenzoic acid (methylmethoxymethylanthranilate) (IV). A new synthesis, by which the constitution is not only confirmed but by which the manufacture of any quantity of the alkaloid is rendered possible, has of late been described by A. Kaufmann and E. Rothlin[6]). They start from the synthetically easily accessible 8-methoxy-

[1]) *Parfum. moderne* **9** (1916), 51. — [2]) *Report* April **1914**, 119. — [3]) *Journ. de Pharm. et Chim.* VII. **13** (1916), 37; *Chem. Zentralbl.* **1916**, II. 74. — [4]) *Report* October **1912**, 84. — [5]) *Report* October **1899**, 38. — [6]) *Berl. Berichte* **49** (1916), 578.

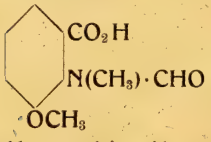
quinoline which, with dimethyl sulphate, yields an addition product from which a considerable percentage of formyldamasceninic acid (III) is obtained by means of potassium permanganate in neutral solution. On boiling with methyl alcohol and hydrochloric acid damascenine (IV) is formed from this acid, along with simultaneous splitting-off of the formyl group and esterification of the carboxyl. For the production of 8-methoxyquinoline they methylate *o*-hydroxyquinoline by treatment with dimethyl sulphate and potash lye in warm aqueous solution, shaking the resulting 8-methoxyquinoline with benzene after over-saturation with alkali; m. p. 46 to 47°; b. p. 164° (14 mm). Methoxyquinoline adds dimethyl sulphate with formation of methoxyquinoline methylsulphomethylate (II). To obtain this salt it is not necessary to isolate the methoxyquinoline. It is sufficient to treat the dry sodium hydroxyquinoline at once with two molecules of the methylating agent. The methoxyquinoline methylsulphomethylate may be oxidized



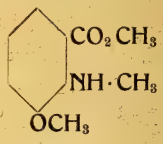
(I) 2-Methylamino-3-methoxybenzoic acid. (Damasceninic acid).



(II) Methoxyquinoline methylsulphomethylate.



(III) Formyldamasceninic acid.



(IV) Damascenine.

to formyldamasceninic acid (III) in aqueous solution with potassium permanganate. The acid is coloured red by admixture of methoxy methylisatine; at the same time some methoxyformylmethylisatinic acid is formed. Formyldamasceninic acid freed from the isatine body melts at 194 to 195°; when heated with dilute hydrochloric acid it is split up into formic acid and damasceninic acid (I). On heating the oxidation lye with diluted mineral acids methoxy-*N*-methylisatine is formed, probably through saponification of the intermediary product, methoxyformylmethylisatinic acid. If, after precipitation and removal of formyldamasceninic acid, the hydrochloric oxidation lye is heated for some time on the water-bath, further quantities of the isatine derivative are separated at first. The filtered solution is then treated with sodium acetate, evaporated to dryness and extracted with ether, when damascenic acid (I) is dissolved. Furthermore, on heating formyldamasceninic acid with a slight excess of hydrochloric acid, the hydrochloride of damasceninic acid, of the m. p. 206 to 207°, is formed. By heating with methyl alcoholic hydrochloric acid damascenine (IV) was obtained from damasceninic acid hydrochloride as well as from formyldamasceninic acid.

Oil of Ocotea usambarensis. In a paper by J. Halberkann[1]) on the occurrence of pseudocubebine in *Ocotea usambarensis*, Engl.[2]) we find a paragraph on the essential oil of this lauracea. It had been obtained from an ethereal bark-extract by distillation in a current of steam, was colourless, became of yellowish colour in the course of time with slight resinifying and had a pleasant smell, resembling rosemary.

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[1]) *Arch. der Pharm.* **254** (1916), 246. — [2]) See Gildemeister and Hoffmann, *The Volatile Oils*, 2nd ed., vol. II, p. 482.

Oil of Olibanum (Frankincense). A number of interesting particulars on the production and the botanical origin of olibanum may be found in a paper by E. M. Holmes[1]). The name of *Olibanum*, by which frankincense is generally known, is derived from the Hebrew word "Lebonah" signifying milk, it being a curious fact that the Chinese word for frankincense ("Ju-siang") has a similar meaning.

The mother-plant was discovered by Carter about the middle of last century and later it was called *Boswellia Carteri* by Birdwood. But there are other kinds or varieties of *Boswellia* yielding frankincense, of which Holmes mentions *B. Bhaw-Dajiana*, Birdw. and *B. Frereana*, Birdw. The Somalis call frankincense *Beyo* or *Hanji-beyo*. There appear to be two distinct species, called by the Arabians *Loban Dakar* (*Mohor* or *Mohur* of the Somalis) from *B. Carteri* and *Loban Maida* (*Yehar* of the Somalis) from *B. Frereana*. The different kinds of frankincense are classed according to colour, size of tears, &c. Carter who travelled in southern Arabia from 1844 to 1846 described the collecting of frankincense and states that the gum is obtained from incisions made during the months of May and December. On its first appearance the gum is as white as milk and soon becomes solid. The species called *Loban Maida (Boswellia Frereana)* is collected in Somaliland, but does not appear to have been distilled as yet.

Oil of Palmetto. A number of years ago Sherman and Briggs examined an oil they had obtained by pressing the berries preserved in alcohol of the palm *Sabal serrulata*, R. et S. (*Serenoa serrulata*, Hook.)[2]). As palmetto oil contains a fair quantity of free acids it was presumed that the ethyl esters found in the oil had been formed in the course of the preservation of the fruits in alcohol. C. A. Mann[3]) who published an exhaustive treatise on the fruit of *Sabal serrulata* has come to the conclusion that the berries contain no, or but traces of, essential oil and that the product which had so far been described as the volatile oil from *Sabal serrulata* had actually been formed by the free acids contained in the berries and by the alcohol used in the preservation of the fruit. He considers it questionable whether such a product should be styled volatile oil from *Sabal serrulata*. The real oil consists of free fatty acids only, the decomposition products of the glycerides of the fat oil. Mann found the following figures for the so-called essential oil: d_{27° 0.8627, n_{D27° 1.4294, acid v. 26.6, ester v. 226.3.

According to C. Griebel and E. Bames[4]) the fruit of *Sabal serrulata* are used for flavouring cognac and are placed on the market in a dried state under the designation of "Bayas negros". They resemble dried plums. A fluid extract is manufactured from Sabal fruit in America which, under the name of "Saw palmetto" is employed in pulmonary diseases. In the flesh of the fruit Griebel and Bames found two enzymes having different actions, one splitting glycerides of fatty acids into acid and glycerol, while the other is capable of partly esterifying the liberated fatty acids with monohydric alcohols.

Oil of Japanese Pepper. Some time ago H. Thoms[5]) had the opportunity of distilling admittedly genuine fruits of so-called Japanese pepper *(Xanthoxylum piperitum*, DC. [N.O. *Rutaceæ*]*)* when 4.33 per cent. of an essential oil was obtained which M. Duruttis[6]) examined more closely[7]). The oil shewed the following constants: d_{20° 0.890, α_D +26.5°,

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[1]) *Perfum. Record* 7 (1916), 78. — [2]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd. ed., vol. II, p. 250. — [3]) Saw palmetto. A chemical study of the fruit of Sabal serrulata. Bull. Univ. Wisconsin N° 767. Science Series. Vol. 4, N° 8. — [4]) *Zeitschr. Untersuch. d. Nahrungs- u. Genussm.* **31** (1916), 282. — [5]) *Arbeiten a. d. pharm. Inst. d. Univ. Berlin* **11** (1914), 58. — [6]) *Ibidem*, 60. — [7]) About earlier examinations of Japanese pepper oil see Gildemeister and Hoffmann, *The Volatile Oils*, 2nd. ed., vol. II, p. 626.

n_D 1.47320. About 90 per cent. of the oil distilled very readily and was collected separately. From a fraction of the b. p. 175 to 177° ($d_{15°}$ 0.8469; α_D + 55.71°) a tetrabromide, m. p. 120°, and a nitrosochloride, m. p. 93 to 95°, were obtained. This fraction evidently contains a mixture of dipentene and *d*-limonene. The terpenes are present in the oil to the extent of about 90 per cent. The portions boiling above 180° were treated with sodium bisulphite; the body freed from the addition product proved to be cuminaldehyde (semicarbazone, m. p. 210°; cuminic acid, m. p. 115°). Free palmitic acid (m. p. 61 to 62°) was present in the portions boiling from 180 to 184°. The oil freed from aldehyde and acids was acetylated; in the saponification liquor acetic acid (analysis of the silver salt) was established. A methoxyl determination of the esterified oil gave a negative result. From a portion boiling chiefly between 106 and 109° (12 mm) ($d_{15°}$ 0.9083; α_D — 7.08°) a solid sodium compound was obtained which, with diphenylcarbamine chloride yielded diphenylurethane of geraniol, m. p. 82 to 83°, which proved that the fraction contained geraniol.

A Japanese pepper oil described by S. Uchida[1]) had somewhat different properties. He calls it "Sansho" oil and states that it was distilled from the dried berries of *Xanthoxylum piperitum*, the yield being 5.7 per cent. 80 per cent. of the oil boiled from 176 to 178°. The pale yellow, readily mobile liquid reminded of citronella oil in odour; $d_{15.5°}$ 0.8504; $\alpha_{D20°}$ + 46° 30′; $n_{D20°}$ 1.4600; acid v. 3.3; ester v. 19.28; after acetylation 23.23. It contained 2 per cent. of free acids (chiefly palmitic acid), 15 per cent. of aldehydes and 77 per cent. of terpenes (chiefly dipentene). The manner in which these constituents were characterized is not indicated.

Oil of Peppermint, American. We would like to mention in this place an "American Peppermint oil" sent us for examination from Switzerland. It shews what kind of "stuff" may be found at the present time in commerce. Although but a very small sample was placed at our disposal, it was large enough to reveal itself as an unmitigated sophistication. This was shewn, to start with, by the ester value which was 186.2, a figure quite out of the question for peppermint oil, the normal figure never being above 50, and reaching 75 only with German oil. The specific gravity likewise was much too high, and only rotation and solubility could be called normal: $d_{15°}$ 0.9483; α_D — 21° 20′; soluble in 1.8 vol. and more of 70 per cent. alcohol, with slight opalescence. As we said before, but little oil was at our disposal, we were therefore restricted to establishing the adulteration only. Evidently the addition of ester was made to produce the impression of a high menthol content.

In an American contemporary[2]) we find a report on the production of peppermint and spearmint oils in the United States, from which we give the following particulars: The annual production of peppermint and spearmint oil in the United States is estimated by the Department of Agriculture at about 250 000 lbs., the world production amounting to about 600 000 lbs. Practically all the American oil is produced in the States of Michigan, Indiana and New York, close upon 25 000 acres being under mint in these States. But there are other localities where mint could be cultivated successfully if the commercial demand for the oil were greater. At the present time prices fluctuate considerably and the entire industry would suffer from over-production if the acreage were to be rapidly extended.

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[1]) *Bull. Forest Expt. Stat.*, Meguro, Tokyo **1915**; *Journ. Soc. Chem. Industry* **35** (1916), 273. — *Chemist and Druggist* 88 (1916), 476. — [2]) *Oil, Paint and Drug Reporter* 88 (1915), N° 23, p. 11.

The Department of Agriculture further states that on the muck lands of Southern Michigan and Northern Indiana, where mint cultivation has become particularly highly developed, the cost of establishing an acre of new mint and caring for it during the first season is placed at about $ 30.—. In subsequent years the cost would be about $ 15.— per acre, but these estimates do not include expenditure for fertilizers, taxes, interest on the land, equipment, superintendence and other overhead charges of similar character. In Wayne County, New York, where peppermint is cultivated on uplands, the cost of preparing the land is somewhat less, but the tillage costs are higher as much more hand labour is required. In the New York district the industry seems to be declining but in Michigan and Indiana many of the growers have invested considerable capital in the business and have provided themselves with an equipment which enables them to handle the product in an economical manner.

The yield of oil per acre varies from almost nothing to nearly 100 lbs. About 325 lbs. of peppermint and 340 lbs. of spearmint are required to produce a pound of oil in commercial practice. The price varies as widely as the yield. For peppermint oil in tins, however, the average price for the last forty years has been in the neighbourhood of about $ 2.50 a pound although it has sometimes fallen as low as 75 cents. Spearmint oil, which used to be a little cheaper than peppermint, has averaged for the past five years about $ 3.65 a pound. It must, however, be remembered, that these prices are somewhat higher than those which the producer would receive.

In Michigan and Indiana the large plantations have, of late years, installed their own distilling plants, many of these being elaborate and expensive. As regards growers who do not have their own distilling plant, the customary charge for distilling their oil has been fixed for many years at 25 cents per pound. The bulk of the mint grown in the United States is distilled in comparatively small plants which usually serve the needs of several growers.

Both peppermint and spearmint thrive best in deep soils rich in humus and retentive of moisture but fairly open in texture and well drained. They may also be grown successfully in well prepared upland soils such as those suitable for corn and potatoes. The area selected should be planted with some plant requiring clean and frequent tillage. The tillage is also continued as long as possible during the growth of the crop, for successful mint growing requires clean culture at all stages. The crop is cut at the time of full bloom which, with new plantings, is usually early in September. It is, as a rule, allowed to dry partially in the field before being hauled to the still. Laboratory experiments show that this practice results in an appreciable loss of oil, but growers do not consider the loss to be sufficient to offset the increased cost of handling and distilling the green herb[1]). Exposure to frost, however, must be avoided, as frozen mint yields scarcely one-half of the normal quantity of oil.

To stimulate the growth of mint nitrate of soda at the rate of 50 to 150 lbs. to the acre is recommended as fertilizer and potash appears to be particularly useful against a form of chlorosis, due, apparently, to an excess of moisture in the soil. On the other hand, ground bone, acid phosphate (see page 44) and lime do not seem to be of marked benefit. Peppermint does not appear to be troubled by many diseases and pests and spearmint is practically free from them all. During very wet seasons a rust fungus sometimes appears and crickets, grasshoppers and caterpillars may do some damage. On suitable soil and with proper cultivation yields of from two to

[1]) Distillation of the green herb has its drawbacks; it lasts longer than with dried herb; moreover, substances pass into the oil which readily oxidize, and which would be rendered innocuous by previous drying. See Gildemeister und Hoffmann, *Die ätherischen Öle*, 2nd. ed., vol. III, p. 551.

three tons of mint herb per acre may be expected. As has already been said, however, the yield of oil is extremely variable and large yields can only be expected from fields that are in the best possible condition. The average for well managed plantings is 30 lbs. per acre. The oil being the chief marketable product, adequate distilling facilities and a market for the oil are essential to the success of the industry and the prospective mint grower should assure himself on these points before investing capital in plantations.

Oil of Peppermint, Hungarian. B. Pater[1]) has published a report on acclimatation experiments carried out in Transsylvania with English mint. Mitcham mint proved to be more aromatic and productive than the Agnelli mint cultivated in Transsylvania so far[2]). Of the experimental field one part was left unmanured, the remainder being divided into plots which were treated with a variety of artificial fertilizers. The favourable effect of manuring is best shewn by the table which we give below; in the first table the fields are classified according to their yield of oil, in the second table according to the amount of herb harvested.

Experiments with artificial fertilizers on Mitcham peppermint fields in Klausenburg tabulated according to yield of oil

Kind of fertilizer	from 67 square fathoms: cc. of oil from fresh herb	Ko. of fresh herb	Ko. of dried herb
1. Acid phosphate + Ammonium sulphate	200	53	13
2. Kainit + Acid phosphate + Chili nitre	189	49	12
3. Chili nitre	189	54	13
4. Kainit + Ammonium sulphate	169	44	11
5. Kainit + Acid phosphate + Ammonium sulphate	162	46	11
6. Kainit + Chili nitre	160	50	11
7. Ammonium sulphate	158	55	12
8. Acid phosphate + Chili nitre	156	42	11
9. Kainit + Acid phosphate	148	47	10
10. Acid phosphate	137	43	10
11. 40 % Kainit	133	42	10
12. Unmanured	130	47	11

Tabulated according to yield of fresh herb

Kind of manure	from 67 square fathoms: Ko. of fresh herb	Ko. of dried herb	cc. of oil from fresh herb
1. Ammonium sulphate	55	12	158
2. Chili nitre	54	13	189
3. Acid phosphate + Ammonium sulphate	53	13	200
4. Kainit + Chili nitre	50	11	160
5. Kainit + Acid phosphate + Chili nitre	49	12	189
6. Unmanured	47	11	130
7. Kainit + Acid phosphate	47	10	148
8. Kainit + Acid phosphate + Ammonium sulphate	46	11	162
9. Kainit + Ammonium sulphate	44	11	169
10. Acid phosphate	43	10	137
11. Acid phosphate + Chili nitre	42	11	156
12. 40 % Kainit	42	10	133

[1]) *Pharm. Post; Seifensieder Ztg.* **43** (1916), 365. — [2]) See *Report* April **1915**, 65.

These fertilizing experiments were carried out on a fresh piece of land, the previous crop having been autumn corn. After the harvest the ground was lightly tilled, manured in the course of the winter and in the spring the mint was planted out after two harrowings. The weather being favourable the young plants grew without watering. Harvesting took place on the 30th. and 31st. of June (?), the herb being left to dry till September on the floor of a drying shed. On a previous occasion bad results had been obtained when the mint herb had been dried at a temperature ranging from 38 to 40° on a hop drying kiln; the herb remained a lovely light green colour, but was completely odourless.

Oil of Petitgrain. In an English contemporary[1]) two Paraguay petitgrain oils are mentioned which, though somewhat weak in odour shewed normal ester percentage (38 to 41 per cent.) but had the unusually high rotation of + 6.8° and + 8° respectively. As no adulteration could be detected the anomaly, in the author's opinion, might possibly be traced to the fact that the material used for distillation contained more twigs than usual or else fruit of greater maturity. He considers it desirable to solve the question by distilling twigs, leaves and unripe fruit separately and to determine the constants of the oils thus obtained.

Anomalies of this description have been met with before now. It was pointed out in 1910 in the above-mentioned journal[2]) as well as by ourselves[3]) that petitgrain oils are met with in commerce which differ from the normal oils in having a lower specific gravity, stronger dextrorotation and lower ester percentage, the odour at the same time being unsatisfactory. At a later date[4]) we were able to supplement this information by stating that these deviations in density and rotation had been observed repeatedly with oils of normal ester content and that in a few isolated cases only stronger rotation had been noticed. The highest rotation observed by us in such oils so far was + 11° 3′. We consider it very probable that the differences referred to are connected with the quality of the material used for distillation, but upon enquiry with the producers we were informed at the time that it was due to unfavourable weather and changed conditions of the soil.

Oil of Pine Needles. It needs no explanation why oils produced in enemy territory are difficult to obtain, or not obtainable at all, in these days. For this reason some of these essential oils have been replaced by more or less successful substitutes, and there is nothing to be said against this practice, provided always that the substitute is sold as such.

It is, however, quite a different thing if it is attempted to "palm off" such substitutes as genuine oils as was the case with two offers of Siberian pine needle oil submitted to us in the course of the last few months. One of these oils (I) had been sampled by a small Leipzig firm, the other (II) by a Wiesbaden firm. In both instances these artificial products had been explicitely called genuine Siberian pine needle oils and the price asked had been adjusted accordingly. The odour alone would have sufficed to betray the products as imitations of a poor quality, and the constants bore this out, as will be seen from the following figures: —

[1]) *Perfum. Record* 7 (1916), 220. — [2]) *Perfum. Record* 1 (1910), 157. — [3]) *Report* October 1910, 107. — [4]) Gildemeister und Hoffmann, *Die ätherischen Öle*, 2nd. ed., vol. III, p. 109.

	sample I	sample II	Siberian pine needle oil
$d_{15°}$	0.8906	0.8919	0.905 to 0.925
α_D	$+6°20'$	$-0°27'$	-37 to $-43°$
Acid value	4.5	0	up to 2.5
Ester value	42.9	46.7	83 to 115
Ester content calculated as bornyl acetate	15 per cent.	16.3 per cent.	29 to 40 per cent.
Solubility in 90 p. c. alcohol	soluble in 3 vol. and more		soluble in 0.5 vol. and more

Sample I had a pronounced odour of pine tar oil, whereas the other sample (II) showed great similarity with certain fractions of wood turpentine oil. Whether the ester of the two oils was really bornyl acetate is more than questionable in view of the result of the analysis; at any rate the sample smelling like pine tar oil smelled hardly of bornyl acetate, and in the other sample the ester appeared to consist of fenchyl acetate which closely resembles bornyl acetate in smell. The samples at our disposal were, unfortunately, too small to permit of closer investigation.

We avail ourselves of this opportunity to report on an adulterated oil of *Pinus Pumilio* supplied by a French firm, and submitted to us by the buyer in Switzerland. Its properties were as follows: $d_{15°}$ 0.8779, $\alpha_D + 5°36'$, acid value 0.6, ester value 3.7, soluble in about 6 vol. and more of 90 per cent. alcohol, with but slight turbidity. The adulteration was easily recognized by the dextrorotation, for oil of *Pinus Pumilio* turns the light to the left ($\alpha_D - 4°30'$ to $-9°$, in isolated cases up to $-15°20'$); moreover the specific gravity was too high and ester value too low. To judge from the odour we had to deal with a mixture of oil of *Pinus Pumilio* with camphor oil and turpentine oil.

These samples may sound a note of warning to buyers, for they show that in these days even such oils are supplied in doubtful qualities in which formerly adulteration was the exception, rather than the rule.

In an article on oil of *Pinus sylvestris* which appeared in the *Pharmazeutische Zeitung*[1]) a short description is given of the process of distillation of the needles or cones of pines and firs in Sweden, Germany, Switzerland, the Tyrol and the United States. Though the report deals with points which are mostly well-known, we may here state that some of the informations given are not quite correct.

Oil of Rose, Bulgarian and Anatolian. We need hardly lay stress on the fact that the War has made the task of reporting exceedingly difficult. From news to hand we gather that this year's distillation was at first carried out under very favourable conditions in the rose districts in Bulgaria, later on however a well-nigh tropical heat set in which considerably affected the yield of oil. We are informed by a reliable source that the average yield was 1 kilo of oil from 3500 kilos of blossoms, the total result of the crop being 2800 kilos of rose oil. The considerable drop, as compared with 3888 kilos in 1915, failed however to exert an appreciable influence on the price which generally speaking remained unaltered at its previous level of about ℳ 1000.— per kilo for irreproachable qualities. As a matter of fact, in consequence of the war the balance of the crops from 1913 to 1915 was still unsold and as export is in a large measure paralyzed an improvement in price is not to be thought of until such time as the article can find its way back to the world's markets by the usual channels, and until the manufacture of *articles de luxe* can be resumed in the normal way.

[1]) *Pharm. Ztg.* **61** (1916), 404.

Distillation of rose oil in Anatolia (Asia Minor), on the growing importance of which we reported on previous occasions, has taken place under conditions similar to those obtaining in Bulgaria. The weather was favourable to start with and the yield of blossoms satisfactory but the yield of oil was greatly reduced by the abnormal heat. Nevertheless about 250000 meticals (*i. e.* about 1200 kilos) of rose oil are said to have been produced. From these facts it will be seen that the efforts made by interested parties in Turkey to further the rose oil industry in Anatolia have met with considerable success. It will require, however, a considerable amount of propaganda work among the rural population to give this young industry the firm foundation necessary for the satisfactory development in its competition with Bulgaria. It is to be hoped that when peace comes the Government will consider it its duty to superintend rose oil production by incorruptible experts and to put a stop, in time, to the importation of the long list of articles used for adulteration purposes. Only in this manner may this new source of production be assured of the success which the experts entrusted with this creation have a right to expect.

The Bulgarian rose oil industry is dealt with exhaustively in an article written by P. Martell [1]) from which we cull a few particulars as a complement to earlier communications on the subject [2]). Historically the beginnings of the rose oil industry as it exists to-day in Southern Bulgaria appear to date back to the times of Ottoman rule; the Turkish geographer Hadii Chalfa reports of extensive rose fields near Adrianople in the first half of the 17th. century and from him we learn too, that rose water was one of the principal articles of commerce of that city. The rose fields in the neighbourhood of Kazanlik appeared only towards the middle of the 18th. century. At the beginnings of the 19th. century we are told of rose fields in the districts of Kalofer, Karlovo, and Klissoura; by the middle of the 19th. century rose culivation had spread to Pechtera and into the district of the Southern Sredna Gora; about ten years ago the rose became acclimatized on the Northern slopes of the Rhodope mountains and a few years ago certain districts on the Northern slopes of the Balkans and in the Struma country also took up rose cultivation.

Besides the damascene and the white rose, the centifolia and the Stamboletz varieties are also met with in Bulgaria, though not to any very large extent. The Stamboletz resembles the damascene rose, and is used for budding the white rose.

The rose selected for oil distillation requires a mild climate and a location protected from north winds. The most suitable soil is clay which must be light and sandy, with a fair admixture of lime and, if possible, deficient in phosphoric acid. A sample of Kazanlik soil examined by Prof. Märker, of Halle, gave the following analysis: 0.10 per cent. nitrogen, 0.26 per cent. lime, 0.64 per cent. of potash and traces of phosphoric acid. The rose grows best in altitudes from 300 to 500 m., but even in higher localities, very good results are met with, such as for instance near Koprishtitza at 1000 m. above sea level. The highest oil percentages are obtained from roses grown on sloping ground, which appear to contain 50 per cent. more oil than those grown in the plains; their price is very high in consequence.

The Bulgarian rose fields have often to suffer from parasites, unfortunately the Bulgarian farmers lack the experience necessary to cope with the evil.

According to Prince Sayn-Wittgenstein who has published an exhaustive study on the Bulgarian rose oil industry [3]) the average yield of one hectare is reckoned to be

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[1]) *Seifensieder Ztg.* **43** (1916), 325, 343, 364. — [2]) See *Report* April **1908**, 86; April **1913**, 89. — Gildemeister and Hoffmann, *The Volatile Oils*, 2nd. ed., vol. II, p. 554. — [3]) It is not stated in the article as to where this study has been published.

about 1400 to 2100 kilos of rose leaves. To produce one miscal (= 4.811 g.) of rose oil about 15 kilos of rose leaves are required (see also page 49 where different figures are given). From this it may be assumed that one hectare will be capable of producing from 93 to 133 miscals. Basing the calculation on the average price obtained in 1909 of 4 francs per miscal, we arrive at an income of fr. 372.— to 532.— per hectare (about 2½ acres).

The description given in the article of the manner in which rose oil and rose water are produced in Bulgaria shews that the destillation method practiced by the Bulgarian rose cultivator is very antiquated and that a number of improvements appear to be necessary[1]).

There are principally two districts in Bulgaria occupied with rose cultivation, *i. e.*, the Southern slopes of the Balkan mountains and the Sredna Gora district, ranging from Sliwen to Panagurichte. Besides, the Northern slopes of the Rhodope range[2]), *i. e.*, the country lying between Pechtera and Stanimaka must also be mentioned in this connection. In many villages rose cultivation represents the chief means of livelihood, as *f. i.* in the village Tekin where 31 per cent. of the cultivated land are rose plantations, in Klissure 25 per cent., in Gorna kissileri 24 per cent., and in Bogas 17 per cent. The price of the rose gardens has been subject to a very considerable rise in the course of the last few years. Whereas about ten to fifteen years ago the price of a ready planted garden was fr. 100.— to fr. 150.— per dekare, this price has now risen to fr. 250.— up to fr. 300.—. Wages are comparatively low, amounting to about fr. 2.— to fr. 2.50 a day for the field and harvest workers.

For many years France was the principal buyer of Bulgarian rose oil; in 1911, however, Germany took the lead, as she bought in this year alone fr. 2723023 worth of rose oil from Bulgaria. Other important customers are England and the United States. Rose water is exported in comparatively small quantities.

About the rose oil business the German Consulate-General in Constantinople reports as under[3]): In consequence of the high prices ruling for rose oil in 1913 many consumers in Europe as well as America took up cheap and synthetic substitutes. Of the 1913 crop about 350000 miscals (1 miscal = 4.811 gr.) were left unsold in Bulgaria and about 30000 miscals in Anatolia. Besides, stocks from previous crops may have found themselves in the hands of dealers and speculators.

The result of the 1914 rose crop of Bulgaria is estimated at 750000 miscals of oil, and 130000 miscals in Asia Minor. As the adulteration of rose oil is now carried on to an unprecedented degree even by the farmers, Anatolian oils were valued higher as far back as 1913, and paid higher than Bulgarian oils, *i. e.*, up to ℳ 3000.— per kilo, as against ℳ 1600.— to ℳ 2500.—. Owing to the outbreak of the war there was no uniformity in the quotations current on the Constantinople market, but the high prices ruling in 1913, based as they were on machinations on the part of speculators, and not on the law of supply and demand, could not be kept up. The average price declined gradually until ℳ 1200.— per kilo was reached.

There are efforts at work to transplant the old Bulgarian rose oil industry in an ever increasing measure to Asia Minor and the success obtained so far is rather promising. But a great obstacle in the way of progress is to be found in the extremely conservative disposition of the village notables and the rural population who look askance

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[1]) See Gildemeister and Hoffmann, *The Volatile Oils*, 2nd. ed., vol. II, p. 554 as well as the map on p. 552. — [2]) The southern districts, the Rhodope range and the Struma district are situated South of the district marked in the map. — [3]) *Nachr. f. Hand., Ind. und Landw.* 1915, N° 86, p. 3 and 4 (see also *Report* October 1915, 33).

at anything new. Besides, the Government has failed to encourage and superintend the industry, so that, it is said, dealers are already busy in putting adulterants in the farmers' hands.

In consequence of the present economical situation an approximately correct estimate of the 1915 production of rose oil is not to be thought of. Interested parties seem to be of opinion that the crop will be 20 to 30 per cent. below the one of the year before. But this decrease is not likely to produce a rise in prices, seeing that there are still old stocks on hand, and that business, as may be expected, is anything but flourishing. So far prices have not been fixed. Some producers and dealers, in want of money, have sold small parcels but the prices obtained by them cannot be looked upon as forming a basis for the market value. At the present time the price for genuine, pure oil is nominally ℳ 1500.— per kilo.

In connexion with this report we would like to give a few particulars from a report published elsewhere on Bulgarian rose cultivation in 1914, according to which the cool weather of the early part of summer delayed florescence, and in consequence the crop and the distillation of the oil[1]). In some of the producing districts, such as *f. i.* Kalofer, the rose plantations suffered from hail and produced an inferior crop of blossoms. In almost all the other districts, however, the crop, according to official reports, has been very good and may be said to have been better than the previous crop both as regards quantity as well as quality. In Kazanlik and Schipka *f. i.*, an average of 17 kilos of white and 12 kilos of red blossoms were required to produce one miscal of oil, in Brezovo 10 to 11 kilos, results which compare favourably with the best years. In Tchirpan one dekare yielded 270 kilos of blossoms: in this instance 10 to 12 kilos of blossoms were required to produce one miscal of rose oil.

In the quinquennial period from 1906 till 1910 the average annual yield of the rose cultivations amounted to fr. 3189046.

Oil of Rose, French. The roses suffered from rainy spring weather and unseasonable snow falls in France[2]). The crop was insufficient for the demand. Rose "Brunner" and "Safranos" were in greater demand than ever before.

The technical process of utilizating garden roses is improved year by year and the oils and extracts obtained from this material meet with an ever-growing demand. Rose water made from garden roses is also asked for steadily.

Oil of Rue. On the occurrence of bergaptene in the fruit of domestic rue and of xanthotoxine in the fruit of *Ruta chalepensis* see page 102 of this *Report*.

Oil of Sandalwood, East Indian. Seeing the present scarcity of stocks, adulteration has become rampant in this article. Of the numerous samples submitted to our laboratories for analysis in the course of the year preceding this *Report* most of them had to be rejected, but we shall only enumerate three of them more closely, their adulteration being proof of extraordinary impudence on the part of the faker.

One of the oils had been sent us from Switzerland and originated from a small Leipzig firm which had sold it "with the guarantee of absolute purity". The following were the constants: d_{150} 0.9811, α_D — 13° 42′, soluble in 4.5 vol. and more of 70 per cent. alcohol, on being further diluted, there was strong opalescence; acid v. 1.8, ester v. 3.7,

[1]) *Chem. Industrie* 38 (1915), 551. — [2]) *Parfum. moderne* 9 (1916), 50.

after acet. 202.5. The rotation is unusually low and the solubility unsatisfactory, for good sandalwood oil gives a clear solution even on further dilution. These anomalies were the more suspicious as a very high content of total santalol is implied by the acetylation value, *viz.*, 93.8 per cent. This induced us to examine the oil more closely when it was found that it was adulterated. This was revealed by the boiling behaviour. Whereas in a pure sample, examined for comparison purposes, nothing distilled over below 280° (757 mm.) the oil under examination began to boil a little above 200° and about 20 per cent. had passed over by the time 280° was reached. This fraction consisted in part of benzyl alcohol[1]), characterized by its conversion into the acetate, oxidation to benzaldehyde and preparation of the phenylurethane (m. p. 77°). It had evidently been added to the oil in order to make it appear rich in santalol, as evidenced by the acetylation value, for every one per cent. of benzyl alcohol creates the fictitious impression of two per cent. of santalol. It is evident, therefore, that acetylation permits of no conclusions being drawn as to actual santalol content in this instance.

The presence of benzyl alcohol, however, does not explain the indifferent solubility, seeing that this alcohol is very readily soluble. It may therefore be taken for granted that this was not the only adulterant present, unless the basis of the concoction was a sandalwood oil of extremely bad solubility, and therefore a very inferior article.

About the same may be said of an oil of French origin which had also been "palmed off" on a Swiss buyer, and which, besides benzyl alcohol, contained glyceryl acetate and terpineol. As also in this case solubility left much to be desired, and as all the above-mentioned additions are readily soluble, it may be left to the imagination of the reader how bad the original sandalwood oil must have been to start with.

The constants of the sample were as under: $d_{15°}$ 0.9800, α_D — 15° 33′, soluble in about 5 vol. and more of 70 per cent. alcohol, strong opalescence on further dilution; acid v. 2.1, ester v. 31.7, after acetylation 206.3. As will be seen, the oil has an unusually high ester value (normally not above 17!) which makes it at once suspicious. The suspicion of adulteration became certainty when it was found that the ester values of the original as well as the acetylated oil decreased to 26.1 and 196.0 when the oil was rectified in a current of steam; for with pure sandalwood oil acetylation value at least does not decrease upon rectification. Closer investigation revealed the presence of several additions, *i. e.* as already stated, glyceryl acetate, benzyl alcohol and terpineol. Glyceryl acetate was eliminated, at least partly, by repeated shaking with weak alcoholic water and recognized after removal of the solvent, *i. a.*, by the high saponification number (514.5). Benzyl alcohol and terpineol passed over in the first fractions upon fractionated distillation. Benzyl alcohol was identified by the phenylurethane, m. p. 77°, terpineol by conversion into its acetate and the nitrosochloride. The latter melted at 105°, exactly as is the case with the preparation obtained from the liquid terpineol of commerce; a mixture of the two nitrosochlorides showed the same melting point.

Needless to say, these additions are made with the object of making the santalol content appear higher, for all the three adulterants are calculated as santalol in the process of acetylation. The ester value after acetylation corresponding to a santalol content of 95.8 per cent. cannot therefore in this instance be relied upon for the real santalol content, which latter is considerably lower. The different adulterants had evidently been selected with a view to balancing specific gravity, which would permit of the admixture being even greater.

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[1]) A similar adulteration had been found by us before now. See *Report* October **1913**, 98.

The third sample took the prize for impudent adulteration, for it was sophisticated in such a barefaced way that it could not have been recognized as sandalwood oil at all, as will be seen from the table below: —

	Sample	Outside figures of pure oil
$d_{15°}$	0.8590	0.974 to 0.985
α_D	$-0°20'$	$-16°$ to $-20°45'$
$n_{D20°}$	1.46983	1.504 to 1.508
sap. value . .	0.5	3 to 25
total santalol .	2.2 per cent.	not below 90 per cent.
Solubility . .	Insoluble even in 96 per cent. alcohol	soluble in 3 to 5 vol. and more of 70 per cent. alcohol

The oil was adulterated with paraffin, and to such an extent that it would have been more correct to designate it as paraffin oil perfumed with sandalwood oil, for there were but traces of sandalwood oil in this mixture.

It is unheard of, and shews an incredible amount of impertinence to bring such a concoction into the market as sandalwood oil. The oil had been offered us from Hamburg but, as was revealed by the label, it originated from Bohemia.

According to A. Chatterton[1]) the "Mysore State Monopoly" realized *R* 1987000.— from the sale of 1862 tons of sandalwood in the administrative year 1913/14. Private concerns are not permitted to distil sandalwood oil in Mysore; on the frontiers of the district, chiefly in the southern Kanara district, the wood is distilled in a small way. Much oil is produced in Kanouj (Punjab). When at the end of 1914, the sandalwood market was very slack in consequence of the war, it was decided to erect an experimental factory for the production of sandalwood oil on a large scale. It is stated that as a result of preliminary experiments a considerable quantity of sandalwood oil has already been distilled which is said to equal European-distilled oil in quality. The sale price was *R* 18.— per lb.

Although sandalwood oil, though of a very poor quality, has been produced in India, from time immemorial, this venture is something quite new, the work being done after a method quite different (?) from the usual way in India. The annual sandalwood auctions will be continued, the new factory buying its sandalwood from the "Forest Department", at the same price other buyers had to pay. If it is found that the industry can be made to pay, it is intended to build a factory large enough to work up the whole annual sandalwood crop of southern India.

Seeing that the English have failed so far to produce a sandalwood oil of a quality satisfying even modest requirements in India, there can be little doubt as regards the outcome of the contemplated venture.

An article published recently[2]) gives a description of the distillation and chemistry of sandalwood oil without however, adding anything new to the subject.

Oil of Spearmint. On the annual production of spearmint oil in the United States see page 42.

Oil of Turpentine. Literature on the desirable exploitation of German Forests for the purpose of obtaining the resin has become fairly voluminous. In the following pages we bring a short resume of the most important publications on the subject.

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[1]) *Mysore Economic Journal; Chemist and Druggist* 88 (1916), 466. — [2]) *Perfum. Record* 7 (1916), 47, 68.

According to a communication by the Board of Agriculture of the province of Brandenburg[1]) the experiments made with a view to utilizing the resin which solidified on the barked parts of fir trees were hardly satisfactory as the resin thus obtained contained but little turpentine oil. On the other hand the endeavours to obtain resin from the ordinary pine have met with more success. The experiments were carried out from the middle of June down to October and produced very favourable results. In spite of the lateness of the start and in the face of unfavourable weather some of the trunks yielded up to 5 kilos of turpentine. In order to produce a larger volume of resin and on a more scientific basis, forest officers of various districts were sent to Chorin where they were made acquainted with the practical part of the work after a process by Kienitz adapted to the conditions obtaining in Germany.

We refer parties interested in the particulars of the Kienitz process to the article in the *Papier-Zeitung*[2]). According to this process which is built up on the experiences collected in the exploitation of turpentine in Russian Poland and in Lower Austria, the trees selected for the purpose are barked by means of a woodman's knife or an axe early in February, in strips reaching from the ground up to about one yard in height, in which process the rough outer bark is removed to a width of about 20 cm.; the cambium, however, must not be hurt. According to its circumference a tree may be made to carry from 3 to 5 of these barked strips. By means of a special tool smooth flat places (called "Lachten") are worked into these strips as near the ground as possible, about 25 cm. high and 10 cm. wide. These special places penetrate the cambium right down to the wood. The instrument used for this purpose resembles a small bent hoe[3]). The exuding resin collects on these "Lachten" and flows downward, into hollows excavated at their lower end by means of a hollow chisel. These smooth, cup-like holes are called "Grandeln". They are from 7 to 8 cm. deep and are further enlarged by a strip of tin, about 15 cm. long and 4 cm. wide being nailed to the trunk in front of them. This work is carried out before the end of April and all the trees selected for the purpose, and which are thus marked out for being cut down later on, are prepared in a similar way.

Resin exploitation is based on the fact that only the rings of the last two or three years carry the gum which exudes after tapping.

About the middle of April the gum appears on the smooth barked places ("Lachten") in the form of small drops flowing gradually into the "Grandeln" (cups). From this time the "Lachten" are cut through every 3 or 4 days to a depth of about 3 to 4 mm. at their upper margin and at the same time they are lengthened in an upward direction. This work has the object of keeping the resin ducts open. When this operation has been done repeatedly, the "Lachten", owing to the gradual evaporation of the turpentine, are covered with a crust of resin which is removed with a scraper from time to time so as to facilitate the regular flow of the gum to the cups. The resin thus scraped off is collected in a suitable bag fixed to the tree in the course of the operation. When the cups are full, the resin is removed by means of an iron spoon and is collected in a wooden vessel called "Stippel". The gum collecting in the cups is superior to the scrape resin which collects on the surface of the "Lachten", it is therefore collected and stored separately, in casks placed into the ground in the neighbourhood of the field of operation. At the end of September the flow of gum ceases, whereupon the "Lachten" are smartly scraped.

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[1]) *Seifenfabrikant* **36** (1916), 78. — [2]) *Papier-Ztg.* **1916**, N° 16; *Seifensieder Ztg.* **43** (1916), 310. — [3]) See illustration in the original publication.

At the end of the first season the "Lachten" have reached a height of about 35 to 40 cm. In subsequent years they continue their extension in an upward direction. Consequently the gum has to cover an ever-increasing length of way, in which process it gets more and more encrusted. In the course of time more and more scrape is obtained, and an ever-decreasing amount of gum. Working the trees for turpentine should be done during the last five years before their being cut down.

It is said that with the pine tree a deterioration of the wood through rot is not to be feared, as has been observed in fir trees as a result of the stoppage of resin exploitation.

In the course of the Chorin experiments the cost of producing one kilo of resin was calculated at ℳ 2.70, a figure which is considerably higher than it would be in a regular exploitation.

An entirely different method of obtaining turpentine, which at the same time permits of a much better exploitation of the turpentine oil contained in the gum, is recommended by H. Wislicenus[1]). He is of opinion that the method practiced so far of obtaining gum in our pine forests must be looked upon as very imperfect; for the pine carries in its wood gum containing about 35 per cent. of turpentine oil of which as a rule little more than one third is recovered under the system now in vogue. From an original pine resin Wislicenus obtained as much as 36 to 38 per cent. of turpentine oil whereas in a fresh flow of resin after an hour, *i. e.* after a day, only a little over 26 per cent. was found and in resin collected after it had been left in the open cups for a few days, but 14 or 15 per cent. (and even less) was contained. Old fir scrape yielded but 3 per cent. of oil upon being distilled. Besides, the resin obtained from the open "Lachten" and cups is invariably mixed with pieces of bark, needles, dirt, insects, &c. &c., amounting to as much at 2 per cent. and more, and necessitating a costly process of purification.

In Austria considerable improvements, after the American prototype of Gilmer's process (which is practically not suitable as yet) were worked out, by Kubelka[2]) and Schmoll who also put them to the test in a purely practical manner, but the difficulties attached to the procuring of the implements required absolutely prevent the general adoption and the economical value of the process, at any rate for the production of turpentine from the common pine.

As in the process recommended by Kubelka, Wislicenus suggests that in a place where the bark is thick, a hole be drilled, about $2^1/_2$ to 3 cm. in diameter, and reaching right through the sapwood into the first layers of the heart-wood and — according to Kubelka — from this aperture two resin ducts should be made with a spiral drill[3]). According to Wislicenus these resin ducts may be just as well drilled tangentially from the outside which is more easily done, at least with the first drillings low down on the trunk, and has, moreover, the advantage of enabling the ducts being kept open from the outside without removing the collecting vessel, and to continue the toppings spirally around the circumference of the trunk. The last two duct drillings are carefully closed with a well fitting cork whereas the neck of a beer or wine bottle is introduced into the first ducts. The bottles keep well in their places from the first but after a day or so they are kept tighter still in quite a startling way by the growth of the incised bark and trunk, and are fitted in air-tight by the exuding and encrusting gum. Within a short time a fairly liquid oily gum of pale yellow colour collects in

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[1]) *Chem. Ztg.* 40 (1916), 559. — [2]) *Österreich. Forst- u. Jagdzeitung* 1915. — [3]) See illustrations in original paper.

the bottles. It contains 36 to 38 per cent. of turpentine oil. Even in well-closed bottles a white deposite is precipitated.

In this process of turpentine production it is absolutely essential that in warm weather the ducts should be redrilled or, better still, that new ducts should be drilled about once or twice a week, for even though the tapping hole be closed to the air the flow of resin decreases mostly on the second day, if the weather be cool, and stops almost completely after three or four days.

Under full exploitation according to this process about 1 120 000 cwts. of turpentine and a round 2 million cwts. of rosin (colophony) could be obtained annually in Germany. The annual consumption of the German Empire is estimated at 1 600 000 cwts. of colophony and 600 000 cwts. of turpentine oil. But little labour is required in the course of production, neither is there any lack of bottles of any kind and description to serve as collecting vessels.

That a similar process is being tried elsewhere is proved by a paper published by C. J. von Dühren[1]) which contains a description of resin production in the Mark districts, where bottles with bent neck are employed[2]).

F. Henrich[3]), in an article on the production of fir balsam (from *Pinus sylvestris*, L.) in the neighbourhood of Erlangen, points out that the collecting bottles are subject to wanton or thoughtless destruction in unguarded parts of the wood. Much turpentine oil is lost owing to the old-fashioned method[4]) of collecting fir balsam in the Erlangen district. To start with, the lower part of the trunk is freed from the outer bark so that a smooth surface of new bark appears without the white inner bark being exposed. As the part of the tree worked in this manner becomes red, the operation is called "the reddening" of the trunk. At the base of the "reddened" strip a piece of about 12 cm. square is freed from the outer and inner bark, *i. e.* from the first layer of wood. With a special instrument the upper margin of this place is cut to a width of about $^1/_2$ cm., down to the depth of one to four annual rings, causing an indentation from the ducts of which turpentine flows. The piece of surface thus prepared, which covers itself with turpentine, is called "Harz-lachte". It ends at its lower margin in a hollow which serves for collecting the gum and is called "Grandel". It is cut at the base of the prepared piece of surface with a special instrument called "Grandel-Eisen" and should not be deeper than 5 to 7 cm. In order to increase the capacity of this excavation a piece of tin is fixed in front of the hole. According to the size of the trunk one or more of these holes are cut into the tree, but with a view to the free circulation of the sap a piece of unaltered bark surface should be left between the various excavations. The gum is removed from the holes daily by means of special spoons. The wood of the last annual ring is cut afresh once or twice a week, the white surface being thus extended at the same time in an upward direction by about 1 to 2 cm. In the course of a vegetation period it increases in length by about 30 to 40 cm.

Henrich distilled 208 gr. of fir resin, the flow of one day, first with ordinary, and subsequently with superheated, steam. Very soon a strongly refractive liquid smelling like turpentine passed over. After this flow had decreased the Florentine flask was changed a first time and a second time when superheated steam was admitted. Fraction I (37 g.), fraction II (13 g.) and fraction III (a few drops only) were thus

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[1]) *Farbenztg.* **20** (1915), 1366. — [2]) See Gildemeister and Hoffmann, *The Volatile Oils*, 2nd. ed., vol. II, p. 64. — [3]) *Chem. Ztg.* **40** (1916), 673. — [4]) In similar manner Austrian (Neustadt) turpentine is obtained. See Gildemeister and Hoffmann, *The Volatile Oils*, 2nd. ed., vol. II, p. 74.

obtained. Altogether 25 per cent. of constituents volatilizable with steam had been removed from the gum. From the first fraction, after repeated distillation, a part was obtained boiling at 153.5 to 154.5°: $d_{4^\circ}^{20^\circ}$ 0.8591; $[\alpha]_{D20^\circ} + 20^\circ$. In fraction I as well as in II α-pinene was proved by the preparation of the nitrosochloride. Presumably the oil contained esters and perhaps also dipentene and sylvestrene.

After an exhaustive historical introduction H. Schelenz[1]), in an article on turpentine oil and resin production in Poland brings a description of resin production in the principality of Lowicz, as it had been communicated to him by the pharmacy manager of the town hospital in Lodz. Since 1908 the Russian engineer L. Wolkow carries on, in the forests of the above-mentioned principality, the production of resin after the French process in a forest area covering obout 5½ hectares. In the first half of May the best spots for cutting are selected in the trees, the spot being called "Brouss" and being situated not far above the main root, the bark being as thin as possible, and the situation to the East or the North. By means of an axe the bark is removed to the extent of about 30 to 80 cm. under the "brouss", below which the trunk is prepared to receive the collecting vessel. Next a hole is cut into the wood, about 0.25 cm. (?) in which a bent tin plate is fitted so as to permit of an easy flow of the exudations. After ten to fifteen days a thin piece is loosened by means of a special hatchet above the hole, a narrow strip is drawn down and diagonal incisions are made in an upward direction which secrete the soft resin and allow it to flow over the zinc plate into the collecting vessel. After about a month, by which time this operation has been repeated about nine times, the collecting vessel is emptied into cases or barrels for export. In 1908 Wolkow obtained by intense work on 428 trees nearly 79 poods (about 1300 ko.), and altogether from 3745 under the most unfavourable weather conditions, 260 poods (about 4200 ko.), besides *Barras* (Galipot).

The resin contained 17 to 19 per cent. of volatile oil and 70 to 75 per cent. of colophony.

Of late years factories were also established in Konsk (Government of Radom) and Skiernevice which were worked successfully although the forests had suffered severely from the depredations of insect pests. The oil is said to be equal to the American product, which, however, seems hardly probable. B. p. 158 to 160°; d 0.8635 (crude oil); d 0.8265 (rectified oil). The chief constituents were α- and β-pinene.

In Konsk oil and colophony of first-class quality are said to be produced. This is also said to be due to the fact that the trees are irritated every three to four days whereby a more liquid exudation is attained, and also owing to the factory, which works without interruption, being situated in closest proximity to the forest under exploitation.

A sample of Polish pine tar oil submitted to the author had the following properties: d_{15° 0.8830; $\alpha_D + 17^\circ$; acid v. 1.5; ester v. 9.3; soluble in about 4 vol. and more of 90 per cent. alcohol. The oil contained a considerable percentage of high-boiling constituents.

Turpentine production has also been described by A. Moye[2]). He deals with the common resin in comparison with the finer kinds having more valuable properties, such as shellac, copal, mastix, and damar. Turpentine as it flows from the tree as a highly viscid liquid is a solution of the resin in turpentine oil. With the exception of the larch-fir all resiniferous conifers produce turpentine just below the bark and

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[1]) *Zeitschr. f. angew. Chem.* **29** (1916), I. 251. — [2]) *Ztg. d. 10. Armee* (Wilna); *Seifensieder Ztg.* **43** (1916), 390. — *Seifenfabrikant* **36** (1916), 478.

in the outer annual rings of the wood. The larch-fir, on the other hand, produces it in the heart-wood.

In conclusion we may here mention an article by C. H. Keutgen[1]) on rosin and its utilization. Keutgen describes and illustrates not only the production of rosin but the utilization of rosin products generally.

A publication by A. Krieger[2]) on the examination of turpentine oil need only be mentioned in a few words as it contains nothing essentially new. As the separation of the reaction-products of sulphuric acid on turpentine oil is not always very distinct, the author suggests that the unattacked parts should be recovered separately by steam, a method which he has not found mentioned in literature and of which he has not heard in practice either. We may point out that this modification was proposed already in 1911 by van der Wielen[3]) and discussed in our semi-annual *Reports*.

Bulletin N° 229 of the United States Department of Agriculture from the pen of A. W. Schorger and H. S. Betts, is devoted to the Naval Stores Industry. This treatise, 58 pages in extent, contains notes on the history of the Naval Stores Industry in the United States, statistical material, speculations on the formation of turpentine in the wood, descriptions of the various tapping and distillation methods in the U. S., &c. &c. The turpentine industry of America is also dealt with. The paper concludes with a bibliography and a review of the American patents granted from the May 17th., 1816 to the February 14th., 1911, and referring to the turpentine industry.

According to a communication from the American Consul in Tegucigalpa (Honduras)[4]), a considerable amount of turpentine oil is produced in that district, and more could be produced if the market conditions were to warrant it. Experimentally the oil has been shipped in iron drums (gasoline tanks), but it was found that the oil is affected by the iron[5]). As much turpentine oil is used in the Panama region, the producers are trying to ship their oil in that direction, but the freights will have to be reduced to make it pay.

From a communication by the London Imperial Institute[6]) we gather that the turpentine distillation plant erected in Shahdara (British India) has been destroyed by floods and that a new factory has been constructed at Sallo railway station, about 8 miles distant from Lahore. From 5600 cwts. of crude turpentine the Shahdara plant had produced 8525 gallons of turpentine oil and 3303 cwts. of colophony during the first eight months of the fiscal year 1913/14, whereas in the year 1912/13 12941 gallons of turpentine oil and 5515 cwts. of colophony were obtained from 7500 cwts. of turpentine. The average price realized for turpentine oil was 2/6 per gallon, and 13/2 per cwt. for the colophony. Tappings carried out in the Rawalpindi and Kangra divisions yielded 11358 cwts. of turpentine in 1913 against 8437 cwts. in 1912.

As regards the turpentine industry in Kumaon, 670000 trees were tapped in the Naini Tal Forest division in 1913/14, yielding 32000 cwts. of crude turpentine, whereas in 1896 only 10000 trees had been tapped[7]).

The manufacture of turpentine products has developed into a considerable industry[8]) in Spain. In 1888 the production of colophony was estimated at 17500000 lbs.; in 1912

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[1]) *Seifensieder Ztg.* **43** (1916), 408, 425, 443, 461, 483. — [2]) *Chem. Ztg.* **40** (1916), 472. — [3]) *Pharm. Weekblad* **8** (1911), N° 35; *Report* April **1912**, 125. — [4]) *Oil, Paint and Drug Reporter* **89** (1916), N° 4, p. 25. — [5]) Presumably the drums were not clean. — [6]) *Bull. Imp. Inst.* **13** (1915), 319. — [7]) See *Report* April **1914**, 95. — [8]) *Bull. Imp. Inst.* **13** (1915), 659.

10959571 lbs. of turpentine oil, 37082445 lbs. of colophony and 69426 lbs. of other products were obtained. The bulk of the production was exported, in 1912 f.i. 7237064 lbs. of turpentine oil and 25067737 lbs. of colophony. The principal buyers were Germany, Great Britain, Switzerland, Australia and the United States, although this latter country produces twenty times as much turpentine than Spain.

The so-called wood turpentine oil, which is obtained from waste wood and fir stumps[1]) by a variety of processes is as a rule looked at askance and is frequently considered to be about on a par with pine tar oil. As a matter of common fact wood turpentine oils of indifferent quality are met with in commerce occasionally, but according to M. Adams[2]) qualities can be produced which resemble genuine turpentine oil in composition as well as in properties. A great mistake is made in bringing wood turpentine oil into the market without any classification whatsoever[3]), the result being that products of every kind and description, good as well as bad, are sold under the same designation.

Adams examined turpentine oils obtained from the wood of the pines occurring in the Western parts of the United States. These are *Pinus ponderosa,* Laws. (Western yellow pine), *Pinus Jeffreyi,* Murray (Jeffrey pine), and *Pinus monophylla,* Torr. (Single leaf nut pine)[4]). The oil was distilled from the wood by means of a retort encased in hot oil, after the process of Adams and Hilton[5]). The distillate was obtained in three fractions, *viz.,* I: b. p. up to 160°, II: b. p. 160 to 220° and III: b. p. above 220°. Only the first fraction was examined. Fraction II contained a considerable amount of decomposition-products which were eliminated by treatment with sulphuric acid, with potash lye and by subsequent distillation by steam. As such a treatment might easily affect the chemical composition of the oil, fraction II and III were not examined.

After rectification by steam-distillation the wood-turpentine oil of *Pinus monophylla* had the following constants: $d_{15°}$ 0.9702 (? 0.8702 ?), $\alpha_{D20°}$ + 21.15°, $n_{D15°}$ 1.4771. It was colourless and had a characteristic, aromatic odour. In a fraction of the b. p. 50 to 60° (15 mm) ($d_{15°}$ 0.8691; $\alpha_{D20°}$ + 29,76°; $n_{D15°}$ 1.4693), amounting to 77.9 per cent. of the oil, α-pinene was found; b. p. 155 to 156°; nitrosochloride, m. p. 103°; nitrolpiperidide, m. p. 118°. tl was impossible to prove the presence of β-pinene with certainty. A small amount of a salt apparently identical with sodium nopinate was obtained, but it was not sufficient for recrystallization. From the fraction b. p. 80 to 135° (15 mm.) ($d_{15°}$ 0.8982; $n_{D15°}$ 1.4856), 9.2 per cent. of the oil, cadinene hydrochloride was produced by the introduction of hydrochloric acid gas, from which the author concludes that cadinene is present in the original oil. From the above particulars it is evident that wood-turpentine oil from *Pinus monophylla* shows great similarity in properties and composition with the oil distilled from the turpentine of the same tree[6]).

In the examination of wood turpentine oil from *Pinus Jeffreyi* special importance was attached to the botanical determination of the wood, seeing that *Pinus monophylla* is difficult to distinguish from *P. Jeffreyi;* many authors consider the latter a variety of the former and it is said that transition forms are known to exist. Seeing that the oils from these two kinds of pines differ considerably in their chemical composition, the examination of the oil from a transition form would be highly desirable. 90 to

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[1]) See Gildemeister and Hoffmann, *The Volatile Oils,* 2nd. ed., vol. II, p. 95. — [2]) *Journ. Ind. Eng. Chemistry* **7** (1915), 957. — [3]) See French and Withrow, *Journ. Ind. Eng. Chemistry* **6** (1914), 148; *Report* April **1914**, 96. — [4]) On the turpentine oil from the gum of the two last named species, see A. W. Schorger, *Journ. Ind. Eng. Chemistry* **5** (1913), 971; *Report* April **1914**, 96. — [5]) *Journ. Ind. Eng. Chemistry* **6** (1914), 378; *Report* April **1915**, 47. — [6]) Schorger, *loc. cit.*

95 per cent. of the wood turpentine oil of *Pinus Jeffreyi* consisted of *n*-heptane (b. p. 99 to 100.5°; $d_{15°}$ 0.6887; $\alpha_D \pm 0$; $n_{D20°}$ 1.3890). The author thinks that limonene and citronellal[1]) are possibly present in the oil, but states that the quantity at his disposal was too small to permit of a closer investigation.

Here too the wood and gum turpentine oil show similarity in their properties and composition.

The wood-turpentine oil from *Pinus ponderosa* had the characteristic odour of the wood of this pine. $d_{15°}$ 0.8626; α_D — 13.15°; n_D 1.4727. The oil contained α-pinene (nitrolpiperidine, m. p. 118°), β-pinene (nopinic acid, m. p. 125°) and limonene (tetrabromide). β-Pinene forms the chief constituent of this oil.

What enormous quantities of waste wood would be available for distillation purposes in the United States is shewn by a paper published by A. D. Little[2]) on the utilization of this waste wood. Of the "long-leaf yellow pine" (*Pinus palustris*, Mill.) alone the annual quantity of waste amounts to about 15 billion feet board measure. If properly utilized, this waste wood would be a richer source of income than the timber itself. According to Little it could be manufactured into turpentine oil, rosin, pine tar oil, tar, varnish, charcoal, ethyl alcohol, ether, woodpulp and pulp boards, paper, paper bags, paper strings, cattle fodder and probably also acetic acid, pyroligneous acid, acetone and producer gas. In his opinion, with an annual production of 15 billion feet of yellow pine there would be sufficient raw material for a daily (?) output of 40000 tons of paper[3]), 3000 tons of colophony, 300000 gallons of "turpentine" oil and 600000 gallons of ethyl alcohol as well as sufficient fuel for all the requirements of these branches of industry.

According to Aschan[4]) the so-called "Finnish turpentine oil" obtained as a by-product when boiling sulphite wood pulp contains up to 20 per cent. of its weight of a new terpenic hydrocarbon, b. p. 163 to 165°; d 0.8628; $[\alpha]_D$ + 7.70°. It seems to be closely related to pinene; no nopinic acid is formed in the course of oxidation.

H. W. Fosse[5]) calls an oil obtained as waste product in the manufacture of wood pulp "Norwegian turpentine oil". We have repeatedly pointed out[6]) that the designation of turpentine oil should be reserved exclusively to the product obtained by steam distillation from turpentine gum and that it is not permissible to call oils such as the one described by Fosse turpentine oil.

The following is the method of producing this "Norwegian turpentine oil": —

Comminuted wood of pine and fir trees is placed in closed iron vessels together with so-called sulphite lye and is boiled at a pressure of 6 to 8 atmospheres, the escaping steam being condensed. In the process of sulphite-boiling, badly-smelling compounds are formed which impart to the crude oil a repulsive odour, but it can be freed from this odour in a large measure by a purification process by hydrochloric acid and chloride of lime.

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[1]) Adams seems to be of opinion that citronellal is present in the turpentine oil from *Pinus Jeffreyi*, as was also assumed by Schorger *(loc. cit.)*. On the occasion of an examination of turpentine oil from *Pinus Jeffreyi* we succeeded in showing that the substance in question is not citronellal, but *n*-decylic aldehyde (*Report* April **1915**, 45). — [2]) *Journ. Ind. Eng. Chemistry* **8** (1916), 102. — [3]) According to a communication in the *Zeitschrift für angewandte Chemie* (**29** [1916], III. 345) 15000 tons of paper are produced in the United States every day. — [4]) *Chem. Ztg.* **40** (1916), 235. — [5]) *Berichte d. deutsch. pharm. Ges.* **25** (1915), 303. — [6]) *Report* April **1905**, 80; October **1905**, 67, 68; April **1915**, 48.

The crude oil had the following properties: $d_{15°}$ 0.8918; $\alpha_{D20°}$ + 7.05°. It contains sulphurous compounds on the nature of which nothing could be ascertained with certainty. α-Pinene was established in a slightly dextrorotary fraction (+ 0.12°) of the b. p. 165 to 170°, forming the chief constituent of the oil, by the preparation of nitrosochloride (m. p. 102°) and the hydrochloride (m. p. 123 to 124°). In a fraction, b. p. 177 to 185°, sylvestrene may possibly have been present. The colour reaction with acetic anhydride did not take place but a hydrochloride was formed, of which the author does not give the melting point, but of which he states that it did not agree exactly with the one of sylvestrene hydrochloride. The examination for cadinene of the fraction b. p. 155 to 220° (18 mm.) produced no result, neither was it possible to prove the presence of substances of the pine tar oil kind by means of the Herzfeld reaction[1]) with sodium sulphite and sulphuric acid.

The rectified oil was nearly colourless. It had the following properties: $d_{20°}$ 0.8717; $\alpha_{D20°}$ + 12.8°.

Pine tar oil, Galician. A few years ago K. Ihnatowicz[2]) published a treatise on Galician pine tar oil of which we give an abstract herewith from the manuscript which the author has kindly placed at our disposal. Galician pine tar oil, which is obtained in Nisko by dry distillation of fir waste wood (from *Pinus silvestris*, L.) possesses an acrid and penetrant odour and a reddish colour. Boiling point 155 to 186°; $d_{15°}$ 0.8828; α_D + 21° 46′; n_D 1.47515; acid v. 6.61. On standing, the oil and to a particularly large extent the parts having a b. p. 50 to 155°, separate a dark brown substance. The oil contains no phenols, but 5 per cent. of aldehydes and ketones. Freed from these constituents it possesses a mild and pleasant odour. Presumably there are also present acetic acid and small quantities of higher fatty acids. Distillation over potassium hydroxide and sodium was rendered very difficult owing to precipitation of brown flocculent masses. Finally a fraction free from oxygen was obtained, b. p. 157 to 158° ($d_{22°}$ 0.8594; α_D + 25° 48′; n_D 1.46757), consisting of *d*-α-pinene; nitrosochloride, m. p. 103°; nitrolpiperidide, m. p. 110°[3]). The fraction b. p. 156 to 166° contains β-pinene, identified by oxidation to nopinic acid (m. p. 128°). In a part boiling from 159.5 to 161.5° ($d_{22°}$ 0.8597; α_D + 24° 51′; n_D 1.46811) camphene was proved by conversion to *iso*borneol (m. p. 211.5°). The parts boiling between 163 and 166° yielded a nitrolbenzylamine m. p. 121 to 122°, which points to the presence of α-pinene. In conclusion Ihnatowicz gives a few particulars on the wood production of Galicia; 26.7 per cent. of the country are covered by woods, 28.9 per cent. of these woods consisting of deciduous trees, 46.3 per cent. of pine and 24.8 of mixed forest. Pines and firs are to be found in the pine woods. Consequently an extensive production of turpentine oil and pine tar oil would be possible. Pine tar oil is produced casually only when parts of forest are cut down. Owing to the importation of Russian pine tar oil and of French and Austrian turpentine oil pine tar oil production has dwindled considerably, it only amounts to about 3000 ko. annually.

According to Berlinerblau a single pine tree produces from 1.4 to 2.5 ko. of turpentine annually from which quantity 18 per cent. of oil can be obtained. Taking an average yield of but 10 per cent., Galicia could supply an annual output of 1800000 ko. of turpentine oil.

On the *use of turpentine oil as a styptical remedy* see page 107 of this *Report*.

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[1]) See Gildemeister and Hoffmann, *The Volatile Oils*, 2nd. ed., vol. II, p. 48. — [2]) *Czasopismo Techniczne* **1911**, N° 23 and 24. — *Chemik polski* **1912**, N° 12 to 19. — [3]) The melting point of pure pinene nitrolpiperidide is between 118 to 119°.

Oil of Vetiver. We may here mention a vetiver oil which had been offered us for sale from Hamburg and which, in the barefacedness of its adulteration may be compared with the gingergrass oil described on p. 32 and the sandalwood oil mentioned on p. 49. The only difference is the kind of admixture. In this case castor oil had been chosen and to such an extent that the sample could not have been recognized as vetiver oil by its constants: d_{15° 0.9654, $\alpha_D + 7^\circ 30'$, acid v. 24.3, ester v. 150.9, insoluble in 80 per cent. alcohol, readily soluble in 90 per cent. alcohol. For comparison purposes we may mention the constants of a pure Réunion distillate, as which the sample had been offered: d_{15° 0.990 to 1.020, $\alpha_D + 22$ to 37°, acid v. 4.5 to 17, ester v. 5 to 20, soluble in 1 to 2 vol. of 80 per cent. alcohol; on further dilution turbidity may be observed occasionally.

As will be seen, all the constants deviate very considerably from the normal, especially so the ester value which points to the addition of fat oil, *i. e.* castor oil, to judge from the behaviour as regards solubility, for castor oil is the only fatty oil which is soluble in 90 per cent. alcohol. In further confirmation of this assumption the sample was tested with light petroleum, when it was found that the oil gave a clear solution at first, but on further addition of the solvent turbidity made its appearance which, after a short time, resulted in the oil separating. Insolubility in light petroleum is specially characteristic for castor oil. Vetiver oil itself is readily soluble in every proportion of this latter solvent.

The quantity of added castor oil could not be determined with certainty, as but a few grams of oil were at our disposal, but the ester value permits at least of an approximate estimate in this direction. Taking the ester value of castor oil as being 180 it follows that the addition must have been about 80 per cent. Judging from the acid value of the sample, which is much too high for a Réunion oil, it may be taken for granted that the sophistication process had an European-distilled oil for its base.

In 1914 1250 ko. of vetiver oil were exported from Réunion at prices ranging from fr. 12.50 to 47.50 per kilo, the annual average value amounting to fr. 40.— per kilo[1]).

Oil of Wormseed, American. On p. 42 of our previous *Report* we had mentioned two samples of American wormseed oil, which bore this designation but otherwise had nothing to do with the real oil, and to-day we may call attention to another batch of such adulterations wich had been sent to our laboratories for analysis in the course of the year. Odour as well as taste betrayed the samples as being utterly different from genuine chenopodium oils, the consfants being also abnormal: —

	d_{15°	α_D	solubility in 70 per cent. alcohol
sample of oil I	0.9262	$-3^\circ 21'$	not soluble in 10 vol.
„ „ „ II	0.9424	$-1^\circ 14'$	soluble in 2.3 vol. and more
„ „ „ III	0.9616	$-2^\circ 25'$	soluble in abt. 2 vol. and more.

Specific gravities and rotations are too low, solubility of oil I is unsatisfactory, whereas with II and III it is exceptionally good. Characteristic constituents of chenopodium oil were not present at all in samples I and II, and but traces thereof in sample III; on the other hand all the three concoctions contained considerable quantities of eucalyptol (up to about 40 to 50 per cent.) which were isolated in the form of the solid resorcinol compound. In samples II and III the presence of anethol could be proved besides, and as regards sample I, its odour pointed to the presence of menthol. Seeing

[1]) *Chem. Ztg.* **40** (1916), 18.

that neither of these bodies occur in genuine chenopodium oil, it was a clear case of mixtures, one of which may have been touched up a little with chenopodium oil.

It is regrettable to see in what unscrupulous, nay, mean manner the faker is wont to proceed, not even stopping at gross adulteration of oils used exclusively for medicinal purposes. As the odour of the oil is familiar to but few buyers and as the simple determination of the constants is in most cases no absolute guarantee for the quality of the oil such unscrupulous actions may remain undetected frequently enough; all the more reason why such conduct should be pilloried.

R. L. Levy [1]) as well as Bishop and Wilson [2]) report on the treatment of ankylostomiasis and hook-worm disease.

Levy gives the following indications as regards ankylostoma treatment in adults: 1st. day: liquid diet, a saline aperient in the morning. 2nd. day: breakfast and dinner are omitted. Saline aperient to be taken at 5 a. m., at 7, 9 and 12 o'clock 16 drops of chenopodium oil each time, taken on a teaspoonful of pounded sugar. At 1 p. m. one oz. of castor oil with the addition of 3 ccm. of chloroform. Dinner consisting of slops.

The author compiles the cases of poisoning known so far in table-form. The majority of such cases were children and in nearly every instance an overdose of the remedy may be suspected. At any rate he recommends American wormseed oil as an efficient, cheap and, in therapeutical dosage, a non-poisonous remedy against ankylostomiasis.

Bishop and Wilson, who prescribe chenopodium oil against hook-worm disease, also recommend a dose of castor oil after wormseed oil. They have found American wormseed oil to be much more efficient than thymol.

We may here point out that we have reported on several occasions on the treatment of worm diseases with American wormseed oil [3]).

On page 42/43 of our *Report* October **1915** we discussed a paper by W. Salant and E. K. Nelson on the effect of American wormseed oil. Further particulars on the physiological properties of this oil are now published by Salant in collaboration with A. E. Livingston [4]). They found that intravenous injections of 0.02 to 0.085 cc. of chenopodium oil per kilo weight caused a reduction of blood pressure with dogs, cats, and rabbits; recovery takes place gradually, after 15 minutes. A second injection of the same amount produces a stronger effect, but if the administration be increased to 0.2 cc. per kilo, no disturbance of the circulation is noticeable. This is more especially pronounced with dogs, less so with cats, and not at all with rabbits. The reduced blood pressure is due to the heart, the kidney volume being decreased along with the depression of blood pressure. Cardiac action is reduced after administration of chenopodium oil, the same may be said of the excitability of the vagus. Chenopodium oil also seems to interfere with respiration; smaller amplitude and reduced activity with breathlessness are likewise a consequence of chenopodium oil. Cats show this effect more quickly than dogs. With rabbits small doses seem to accelerate respiration and even after big doses breathlessness is rarely observed. Even after intravenous injection of 0.02 to 0.024 cc. per kilo or administration of 2 g. per kilo in the stomach or the small intestine of the cat neither methæmoglobin nor hæmolysis occurred. It is surmised that the cause of slackened respiration and breathlessness is due to

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[1]) Journ. Americ. Med. Assoc. **63** (1914), 1946; Therap. Monatsh. **29** (1915), 633. — [2]) Journ. Americ. Med. Assoc. **65** (1916), 19; Chemist and Druggist **87** (1915), 767. — [3]) See *Report* October **1906**, 81; April **1907**, 102; April **1910**, 121; October **1910**, 143; April **1911**, 121; October **1913**, 108; April **1914**, 99; April **1915**, 50. — [4]) *Amer. Journ. Physiol.* **38** (1915), 67; *Chem. Zentralbl.* **1915**, II. 1082.

oxygen being liberated in the system by the ascaridol. The effect of chenopodium oil on respiration is independent of the effect on circulation. The *dosis tolerata* of chenopodium oil in intravenous injection varies with the different animals, the average amounting to between 0.03 and 0.35 cc. per kilo body weight with cats, dogs, and rabbits. The slight depressive effect of chenopodium oil on the respiration of rabbits is ascribed to the higher content of carbonic acid of the rabbit blood.

The influence of chenopodium oil on the contractibility of the bowel is discussed in a paper by Salant and C. W. Mitchell[1]). Given in the form of Locke's solution[2]) chenopodium oil causes a distinct and lasting tonus decrease in the isolated rabbit bowel, and reduces the frequency and strength of the contractions. This, however, disappears after 20 to 25 minutes. In Locke's solution free from oil recovery sets in. In carnivores American wormseed oil mostly causes a tonus increase, followed by subsequent lasting decrease. The rhythmical contractions increase in frequency but disappear finally. Here, too, in solution free from oil recovery sets in. The reaction after chenopodium oil was most pronounced in the colon and was greater than in the ileum and jejunum. Caffein does not act antagonistically, it increases, however, the tonus reduction. Neither are barium chloride and pilocarpine antagonistical, but, added previous to administration, they act retardatively on the tonus depression. After poisoning with chenopodium oil pilocarpine is without effect, on the other hand barium chloride decreases the tonus. Comparatively large doses of chenopodium oil are required in intravenous injection with rabbits in order to decrease the peristaltic movements. The authors presume the presence of antagonistical bodies.

In a lecture on intestine parasites given in Rostock, Brüning[3]) gave a few particulars on the treatment of oxyuris disease. The removal of the worms from the rectum can be effected by irrigation with a solution of 15 to 25 drops of chenopodium oil in one litre of water. In the treatment of round-worms the oil may be used as successfully as santonine.

Oil of Wormwood. The legislation relating to absinthe[4]) has hit certain districts of France very severely. Cultivation of wormwood was looked upon as the principal source of income in many places, such as *f. i.* in the little town Orly in the district of Ivry-sur-Seine which was almost exclusively dependent for its livelihood on the income derived from this source[5]). In order to indemnify the cultivators for their considerable losses the whole of the wormwood crop was bought by the Government and destroyed. In Orly alone wormwood cultivations of a value of fr. 100 000.— were thus destroyed in the course of a few days. It appears that the same was done in the districts of Houdan, Milly, Orsay and in several other places besides.

Oil of Xanthoxylum ailanthoides. The rutacea *Xanthoxylum ailanthoides*, Sieb. et Zucc. (Japanese "Karasu-Zansho") is indigenous in southern Japan. For the oil from the leaves, which is of a light greenish-yellow to orange-yellow colour, Y. Shinosaki[6]) gives the following constants:

For the oil from mature leaves: $d_{15°}$ 0.8437; α_D — 6.35°; $n_{D20°}$ 1.4474; acid. v. 0.94; sap. v. 2.81; after acet. 20.53; sol. p. + 3°.

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[1]) *Amer. Journ. Physiol.* **39** (1915), 37; *Chem. Zentralbl.* **1916**, I. 803. — [2]) Locke's solution contains 0.03 per cent. of calcium chloride, 0.9 per cent. of sodium chloride and 0.04 per cent. of bicarbonate of soda. — [3]) *Zeitschr. f. ärztl. Fortbildung* **13** (1916), 373. — [4]) See *Report* April **1907**, 103; April **1908**, 119; April **1909**, 92. — [5]) *Chemie, Ztg. f. d. ges. chem. Ind.* **8** (1915), N° 2006 to 2010 of Nov. 15th. — [6]) *J. Chem. Ind. Tokyo* **18** (1915), 1077; *Journ. Soc. Chem. Industry* **34** (1915), 1270.

For the oil from semi-mature leaves: $d_{15°}$ 0.8385; α_D — 5.75°; $n_{D20°}$ 1.4408; sap. v. 4.21; after acet. 14.96; sol. p. + 2.5°.

For the oil from young leaves: $d_{15°}$ 0.8390; α_D — 6.63°; $n_{D20°}$ 1.4440; acid v. 0.4; sap. v. 1.83; after acet. 1.68; sol. p. 0°.

The principal constituents of the oil are methyl-*n*-nonylketone, terpenes and about 1.5 per cent. of phenols. Nothing can be gathered from the report as to the proof of the ketone.

Oil of Xanthoxylum piperitum, see page 41.

Oil of Yamakosho leaves. From the leaves of the Formosan *Yamakosho* plant Y. Shinosaki[1]) obtained 1.2 per cent. of a brownish-yellow oil of camphory smell. $d_{15°}$ 0.9049; α_D — 18.8°; $n_{D20°}$ 1.4635; sap. v. after acet. 48.66; insoluble in 70 per cent. alcohol. 90 per cent. of the oil boil from 160 to 190°, 6 per cent. between 190 and 205°. It contains about 33 per cent. of hydrocarbons and about 49 per cent. of cineole (resorcinol method).

Nothing is known as regards the botanical origin of the *Yamakosho* leaves.

Oil of Ylang-Ylang. Of this oil about 20000 kilos were exported from Réunion in 1914, which is a little more than the year before. The prices varied between fr. 50.— and fr. 60.— as against £ 6.— in the preceding year[2]).

On page 109 of our *Report* October **1913** we discussed a paper by Jahrling on the classification of ylang oils according to their constants and we came to the conclusion that it would not be advisable to accept Jahrling's outside values for the various qualities (extra, I^a, I^b, II), as in our experience they are not to be relied upon in judging best oils of commerce. We said at the time that the evaluation of ylang oils was not by any means such a simple matter as it would appear from Jahrling's publication and we can only repeat this statement in view of a paper by H. D. Gibbs[3]) which may be looked upon as a continuation of Jahrling's theories and in which the same standpoint is taken up. Gibbs has examined quite a number of ylang oils originating in part from the factory of Santos & Jahrling and has collected the analytical results in two tables. Here again classification took place exclusively according to the constants, more especially the ester value, a measure which, after our own observations, we are simply unable to accept. The following properties were found in the various qualties examined: —

Quality	Number of oils examined	$d^{30°}_{30°}$	$\alpha_{D30°}$	$n_{D30°}$	Ester v.
Extra	10	0.9478 to 0.9612	— 6.7° to — 27.5°	1.4762 to 1.4900	148.2 to 201.7
I^a	15	0.9292 to 0.9472	— 16.75° to — 45.95°	1.4835 to 1.4965	122.0 to 143.0
I^b	2	0.9349 and 0.9255	— 32.2° and — 46.2°	1.4935 and 1.4975	112.7 and 115.2
II	1	0.9127	— 51.4°	1.5040	61.3

[1]) *J. Chem. Ind. Tokyo* **18** (1915), 1081; *Journ. Soc. Chem. Industry* **34** (1915), 1270. — [2]) *Chem. Ztg.* **40** (1916), 18. — [3]) *Philippine Journ. of Sc.* **10** (1915), A, 99.

Gibbs considers the determination of solubility a very useful criterion as it would permit of conclusions being drawn as regards sesquiterpene content of the oils. The "extra" quality dissolved in half its volume of 80 per cent. alcohol, the I^a quality in half its volume of 90 per cent. alcohol. (It is not stated whether per cent. by volume or by weight is meant.)

Nothing is altered in our opinion as regards evaluation of ylang oils by what Gibbs has published, so that we need only refer to what we wrote in the *Report* referred to above. But we would like to emphasize once more that we have never been able to observe, in ylang oils of the very best class, all the properties which Gibbs indicates for the qualities "extra" and "I^a". On the contrary, we have it on record that just the oils with particularly high ester content had to be classed as inferior on account of their indifferent odour. That is reason enough for us to refrain from accepting Jahrling's and Gibbs' opinion without more ado.

Gibbs gives the following table of exports of ylang oils from the Philippine islands from 1909 to 1913: —

	Quantity in kilos	Total value Pesos[1])	Price per kilo Pesos[1])
1909	2812	175 872	62.54
1910	1878	116 668	62.12
1911	1684	94 808	56.30
1912	2785	161 758	58.08
1913	2172	116 618	53.70

Chemical Preparations and Drugs.

Oil of Almonds, expressed. Communications of general interest, of which we give a short abstract herewith, are published in an article by the London Imperial Institute[2]) about the almond tree. The common almond tree (*Prunus Amygdalus*, L. = *Amygdalus communis*, Stokes) is a member of the N. O. *Rosaceæ* and reaches a height of 15 to 25 feet. There are two classes of almonds, known as sweet and bitter almonds (*Amygdalus communis dulcis* und *A. c. amara*), but no botanical difference has been found to exist between either trees or fruits. It seems probable that in its original state the almond was bitter and that the sweet variety, occurring first as a "sport"[3]), became established by cultivation.

According to De Candolle the almond is indigenous to Asia Minor, Persia and Syria, and perhaps parts of Greece. Even at the present day a truly wild bitter almond tree is stated to occur in Palestine in such numbers that the kernels form an important article of commerce, being collected by Bedouin women and taken into Damascus.

The most important almond-producing countries are Spain, Portugal, Morocco, Sicily, France, Canary Islands, Italy, Sardinia, Syria, Persia and Southern California. The almond tree was introduced into the latter country in 1885 and since then has been grown quite successfully. Cultivation has become distinctly profitable in certain

[1]) 1 Philippine Peso = 50 American cents = ℳ 2.10. — [2]) *Bull. Imp. Inst.* **13** (1915), 460. — [3]) A variation or aberration.

valleys of the State although difficulty has been experienced in finding localities whose climate suited the tree.

Sweet almonds are cultivated principally in Spain and Southern California. The Spanish industry is centred in the districts around Malaga, Valencia and Alicante. In France almonds are grown in Provence, the chief marketing centre being the town of Aix. Italian almonds are produced mainly in Sicily and the districts round Bari. Of late years, almonds cultivation has been taken up in Sardinia. Bitter almonds are obtained very largely from North Africa, particularly Mogador.

Numerous varieties of the almond, especially of the sweet almond, are known in commerce; they differ principally in the thickness of the shell, delicacy of flavour of the kernel and thickness of the testa. Some of the best-known European varieties are the Jordan, Valencia, "Princess" (remarkable for its very thin shell), Languedoc, "Douce à coque dure", "Sultana", and "Pistache". Varieties cultivated in California are the "Excelsior", "Non plus ultra", "Nonpareil", "Il Suprema", and "Commercial".

The almond tree flourishes best in subtropical regions which possess a small but sufficient rainfall, and where nothing more than a very slight frost is experienced during the flowering season (January or February). It also grows well in the warmer districts of the temperate zone but as the almond blossoms appear early in the year, they are often injured by frost. In the tropics the almond tree, whilst apparently flourishing, usually becomes partly or wholly sterile, presumably in consequence of the excessively moist climate.

In the vicinity of Malaga, where the well-known Jordan almonds are grown, the climatic and other conditions are apparently ideally suited for the cultivation of this variety, since it cannot be grown with equal success in any other district of Europe. Owing to bad seasons, however, and fungoid diseases Malaga now only occupies a secondary place in almond culture, Valencia almonds now being grown over a much larger area.

The almond tree flourishes best in a deep, warm, dry and, if possible, very chalky soil, affording some shelter from the prevailing wind.

In Spain most of the almond trees are either budded or grafted, the stock employed being usually of the bitter variety. The finest almonds are selected and placed in layers in wet sand in the autumn. In the following spring they are sown about two inches deep in light, rich soil, being placed about a foot apart, with a space of two feet between the rows. At the end of the same summer the young plants may be budded. As a rule, however, the almond is trained as a standard or half standard, in which case the seedlings are allowed to grow for a year or two longer, when they are grafted at a height of from 2 to 4 ft. above the ground. In the spring following the budding or the grafting the young trees are cut back and planted out in their permanent situation. In order to obtain good crops the tree must be pruned yearly and kept well manured.

The method of harvesting is very simple. When the fruit is ripe the pericarp opens, the almonds are knocked off with light rods, the nuts separated from the dry pericarp and spread out to dry. They are exported either in their shell or else cracked by hand, usually by women and children. In the latter case the kernels are taken down from the villages to the local buyers, who send them to the shipping warehouses, whence they are exported after having been carefully graded.

In Italy the almond trees begin to bear at four years old, reaching full bearing at about fifteen years. The average yield of a tree is stated to be about 9 lbs. of shelled almonds, where soil and climatic conditions are in every respect favourable.

The export of almonds from the principal countries of production are as follows: —

	1911 Cwts.	1911 £	1912 Cwts.	1912 £
Italy	365 600	1 600 000	452 600	2 062 000
Spain	291 260	1 048 000	185 600	635 000
Morocco	56 540	232 124	42 280	169 481
California	—	—	60 000	—

As has already been mentioned, the almond tree grows in the protected valleys of Palestine, where a number of other fruit-bearing plants are also cultivated. From an article by J. Aharoni[1]) we gather that the cultivation of the almond tree is not always free from trouble, for the article deals with a newly-discovered noxious insect, of a kind of *Eurytoma (Chalcididæ)* which in the course of twenty years has destroyed more than 50 per cent. of the almond fruit. The punctured almond first turns yellowish, then brown and finally becomes black by degrees. This pest can only be fought by taking down and burning all the affected fruit. The occurrence of this unknown *Eurytoma* kind as almond tree pest is particularly interesting, for of this genus only species of the parasite kind were known so far.

Towards the end of the blossoming season of the almond trees, *i. e.* from about the end of February to the beginning of March the *Eurytoma* emerges fully-grown from the fruit and at once sets to work in puncturing the seed buds of the growing almonds. The mother-insect seems to know of the growing fruit, whether it will contain one or two kernels, for in all almonds containing two kernels there are invariably two larvæ or fully-grown insects to be found. The author has not succeeded in finding the egg. The larva is white, without eyes or feet and also lacks distinct outlines of a head. The wrinkled body tapers at both ends, only the middle being distended belly-like. When squashed, a greenish juice exudes from the body, even from those feeding on kernels which have long become white. The larva seems absolutely indifferent to climatic conditions and appears to have no natural enemies, which may account for the fact that the growth of this pest has become absolutely overwhelming since almonds were first cultivated in Palestine (*i. e.* about 23 years ago in Rehoboth near Jaffa). It is not known on what fruit they lived before the introduction of the "Victoria" and "Princess" almonds, which they seem to prefer on account of their softer shells. In Arabian almonds with hard shells Aharoni found quite different kind of pests. By the time the almond harvest is due (from the middle of July to the beginning of August) the kernel is completely devoured. The larva assumes the chrysalis stage in spring, this form lasting about two weeks. The author gives no particulars about the appearance of the fully-grown insect, except that it is shining black and has red eyes.

When, in the early stages of the war, lack of fat was predicted a variety of sources of oil, most of them half-forgotten, were called to mind, and it was recommended more especially to collect the seed from pumpkins, sun flowers, grapes, as well as the beech-acorn and the seeds from apples, pears, plums, quince, &c. Furthermore the cultivation of oil fruit was extended very considerably, the result being that this year we may rely on a largely increased amount of oil being available for consumption purposes. But in comparison with the consumption of oil in times of peace the quantities are insignificant. It is, therefore, imperative that all oil fruit and oil seeds should be utilized for the production of oil. In 1915 the collecting of the stone-

[1]) *Tropenpflanzer* **19** (1916), 317.

fruit seeds was not comprehensive enough. In many parts the collected seeds were left unused and were exposed to rot and destruction because few, if any, of the oil millers were disposed to work them for oil. The reason was the large percentage of useless shell, amounting to from 70 to 90 per cent., and even more in the case of peach kernels. Mereover, no economically practicable process of removing the shells from the kernel was known.

This state of affairs has induced K. Alpers[1]) to study the question of facilitating the production of oil from seeds of stone-fruit. That the endeavours to utilize these oils are of particular interest he proves by the following calculation. According to the census of 1900 the German Empire possesses 21.5 millions of cherry and 69.4 millions of plum trees. From literature on the subject as well as from his own experience the author found that cherries have about 5 per cent., prunes and apricots about 10 per cent. of stones. Cherrystones yield about 30 per cent., plum and prune stones about 15 per cent. and apricot stones about 25 per cent., peach stones about 7 per cent. by weight, of oil kernels. Cherry kernels contain about 36 per cent., plum kernels about 42 per cent., peach and apricot kernels about 47 per cent. of oil. Needless to say, these figures only hold good for best selected kernels, the average figures being smaller, seeing that a fairly considerable percentage of the stones contain kernels of indifferent quality. Nevertheless, given a fair average crop, several million kilos of oil could be obtained from stone-fruit in Germany. The stones obtained from fruit exploitation and from distilleries could without difficulty be sent to the oil millers; smaller quantities, collected in individual households, would be gathered by school children as far as possible, and in this manner a large part of the stones of stone-fruit could be made use of.

Alpers has tried to find a process for separating the shells from the kernels in a commercially practicable way, so as to eliminate the high cost of carriage of the shells, and to be able to press the oil in every kind of oil mill.

In all probability no machines for cracking the stones of stone-fruit have ever been used in Germany. The author knows of but one factory where it was tried to build machines for cracking plum stones; similar machines for hazlenut cracking as well as some machines for cracking almonds, have been supplied to foreign countries. These machines might be made use of for cracking cherry and plum stones. Alpers has tried sorting machines for separating the cracked shells from the kernels after he had convinced himself that picking the kernels by hand was out of the question. By means of a coffee-sorting-machine it was found possible, in the case of cracked cherry stones, to separate the major part of the round cherry kernels, so that, in view of the prices now ruling for oil, the use of these machines might possibly prove of value with cherries. However, the author did not continue his experiments with sorting-machines, as he had meantime found another way for separating the shells from the kernels.

The specific gravity of plum kernels amounts to 1.05, that of the shell to about 1.18; with cherry, apricot and peach stones the case is similar. It is therefore possible, by means of a calcium chloride or chloride of magnesia solution of a density of about 1.15, to separate the kernels of cracked cherry, plum and apricot stones almost completely from their shells. In such a solution the kernels float on the surface whilst the shells sink. The kernels can be removed with a sieve, after which they are washed, dried and pressed. The process has the advantage of being practicable on a large scale.

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[1]) *Chem. Ztg.* 40 (1916), 645.

Alpers carried out the separation of the kernel from the shells with 87 kilos of a mixture of plum and prune stones of different kinds with complete success. The plum stones were cracked in a hand mill used for comminuting stones and similar substances. In this process about half the kernels remained unhurt. 11.5 kilos of kernels were obtained with but a slight admixture of shell parts. The kernels, when ground, showed 30.96 per cent. of oil and 9.92 per cent. of water, and yielded 2.52 kilos of oil upon pressure. Cherry as well as apricot stones were treated with equal success, though in smaller quantities, the shells being separated from the kernels. The majority of the shells sinks to the bottom of the chloride of magnesia solution almost immediately upon its being stirred; the lighter parts of the shells get saturated with salt solution upon standing and sink for the most part after a short time. In the height of summer the washed kernels may be dried in the open air.

When the intact kernels are placed in salt solutions, little or but traces of dissolution and decomposition of the amygdaline can take place; on the other hand if the kernels are thoroughly crushed it might happen that, of repeated additions of such kernels are made to the solution, sufficient hydrocyanic acid might find its way into the liquid to affect the health of the workmen. By frequently changing the cheap solution and by working in an open shed this possibility might be counteracted successfully. Alpers himself reports that though he treated several cwts. of plum stones in the above manner, the kernels of which had become partly comminuted, he felt no bad effect.

The oil pressed from the kernels, which had been partly comminuted and treated in the magnesium chloride solution, was somewhat turbid to start with, but it soon became clear. It had a mild and pleasant though somewhat bitter taste and smelled strongly of bitter almond oil. In salads prepared with it, taste and odour of bitter almonds predominated, and persons who tasted the salads pronounced it to be an uncommon, though not exactly unpleasant taste. Odour as well as taste of bitter almonds were, however, easily eliminated by distillation with steam. After this treatment the oil had a fine and delicate flavour. Heated to 160°, or after standing in an open bottle for a fortnight, the oil was almost odourless. The heating had not affected its quality either. In the steam distillate from 100 g. of oil 4 mg. of hydrocyanic acid were proved to be present.

J. Merz[1]) is of opinion that he has solved the question of exploiting stone fruit kernels in a different, and, as he believes, far more rational manner. According to his process the stones are disintegrated and the resulting mass is extracted. In this manner the whole of the oil contained in the mass is recovered free from hydrocyanic acid on account of the steam process in recovering the solvent. The residue, freed from the oil, is finely ground and the resulting meal may be used for feeding cattle. The kernel meal may be separated from the shell parts by means of a special blast-sifter, without previous grinding of the mass freed from the oil. The oil thus obtained may be refined to a culinary oil of irreproachable quality, same as all extracted oils.

Ambergris. On Ambergris and its examination Ch. Bruff[2]) has published a short treatise which we reproduce herewith: — Most of the Norwegian whaling companies have their fields of activity in the Antarctic Seas where they hunt chiefly the blue whale and other cetaceans. Some of the companies have their districts along the African

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[1]) *Chem. Ztg.* **40** (1916), 716. Further particulars on new sources of oil may be found under this heading in an article published in the *Zeitschrift für angewandte Chemie* [**29** (1916), I. 337]. — [2]) *Tidsskrift for Kemi Farmaci og Terapi*, Kristiania, 1. May 1915, N° 9, page 125.

coast and in other tropical seas where their attention is devoted to the *Physeter macrocephalus*, the spermaceti whale or cachalot, known as being the biggest cetacean, and from which the valuable substance ambergris is obtained.

Norwegian chemists are often called upon to decide whether the ambergris brought back by the whalers is genuine or not. Ambergris is formed in the bowels of above-mentioned whale, but as it is not found in every animal captured its presence may possibly be due to a disease.

In some instances the animal ejects the ambergris in lumps of from 1/2 to 75 kilos, and as the specific gravity of ambergris is well below 1, these lumps keep afloat for some considerable time, and they often drift ashore in the seas frequented by the whale.

The transverse section of ambergris shows a concentrical formation of layers of dark or light colour, ranging from greyish yellow to brownish black. The whole lump is permeated with the horny beak-like jaws of a cuttle-fish species which serves as food to the cachalot, and the presence of which in the ambergris is characteristic for genuine ambergris. These horny jaws resemble the beak of a parrot, they are dark brown in colour and thin.

The publications which appeared so far on the chemical and physical properties of ambergris are rather incomplete. The melting point is given as being 60°. An experiment shows that ambergris is converted but very slowly from the solid to the liquid state. At 60° it is paste-like, but not liquid and it may be heated much beyond this degree before it assumes liquid form. Specific gravity is said to be from 0.908 to 0.920. An experiment showed a specific gravity of 0.950, but the sample under examination had been softened and compressed by the warmth of the hand. As regards the chemical composition of ambergris it is said to consist of about 85 per cent. of a fatty substance (ambraine) and about 13 per cent. of ambergris oil besides small traces of mineral substances. The fatty constituent of ambergris is not a fat but, according to Hammarsten, a high-molecular monohydric alcohol resembling cholesterol ($C_{26}H_{43}OH + aq$). As it forms the chief constituent of ambergris, the saponification value of the latter is low. With three samples values of 17, 19 and 35 respectively were found[1]). In consideration of the very high cost of the substance the experiments were carried out with but 0.2 g. in each instance. The residue of ashes is but small, only traces of ashes being left on the platinum dish on combustion. Ambergris is adulterated with tallow, benzoin, frankincense, wax &c., which substances are perfumed with genuine ambergris or musk.

Ambergris was used formerly in medicine in the form of tincture as a sedative in hysterics and against spasms. To-day its principal use is in perfumery as a fixing agent for other perfumes. Its price is, as will be known, very high, being about 4000 kroner (Scand. currency) per kilo, and in a retail way about 4 1/2 kroner per gram.

Persons entrusted with the analysis of ambergris should convince themselves in the first place of the presence of the beak-like cuttle-fish jaws, and of the formation in concentrical layers. Next it should be ascertained whether the residue of ashes is small and saponification value low. Specific gravity and melting point afford no reliable indications for an analysis.

Benzyl benzoate. The Earl of Berkeley[2]) has found that, when producing benzyl benzoate after Claisen's process[3]) (heating of sodium, benzyl alcohol and benzaldehyde

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[1]) According to Riban (*Compt. rend.* **154** (1912), 1729; *Report* October **1912**, 118) ambraine is a body of the composition $C_{28}H_{40}O$. — [2]) *Journ. Chem. Soc.* **109** (1916), 522. — [3]) *Berl. Berichte* **20** (1887), 649.

on the water-bath for several days) the yield may be considerably increased and the duration of the process shortened if freshly distilled and entirely dry benzaldehyde and benzyl alcohol are used. The Earl dissolved 2.3 g. of sodium in 30 cc. of benzyl alcohol and poured the solution, while still boiling, gradually into 300 cc. of freshly distilled benzaldehyde. After heating for 24 hours on the water-bath the substance was further treated, when about 285 cc. of benzyl benzoate were obtained. No smell of benzaldehyde was observed in the course of this process.

Cinnamaldehyde. A colorimetric process for determining cinnamaldehyde in cinnamon will be found described on page 92 of this *Report*.

Coumarin. Communications of general interest concerning the collecting and curing of tonka beans are given in a treatise by E. Albes[1]). As will be known the tonka bean is the seed of *Dipteryx odorata*, Willd. (*Coumarouna odorata*, Aubl.)[2]), a tree belonging to the *Leguminosæ* or pulse family and growing from 60 to 90 feet high in tropical South America generally. The best beans come from the region between the Caura and Cuchivero rivers, in Eastern Venezuela, where the soil seems to be most favourable for the growth of the tonka bean tree. The trees are not usually found in groves, but grow singly, though small clumps are occasionally met with. The gathering of the nuts is thus all the more difficult and arduous. Cultivation of the tree has been attempted in Trinidad and other parts of the West Indies, but as it takes from 10 to 12 years for a tree to come into bearing this has apparently discouraged the planters and the wild product is still depended upon to supply the markets. Again the crops seem to be very irregular. As a rule there does not seem to be more than one good crop in three years, production in the interval being so small that it hardly pays to collect the beans.

In Venezuela the tree is known as *sarrapia*, the men engaged in the collection of the seeds being called *sarrapieros*. Ciudad Bolivar is the centre of the tonka-bean industry.

Birds, especially of the parrot family, frequently cause considerable damage. They feed on the small immature fruit of the trees in the months of October and November, long before the beans are ready to be gathered. Where these birds have eaten the ground is strewn with fruit only clawed and then awkwardly dropped, or perhaps with just a small piece bitten off.

About the beginning of February the *sarrapieros* begin to organize their expeditions to the interior to collect the beans. For two or three months thereafter the Caura River is animated with boats of every kind or description, some of them carrying entire families on their way to the districts where the trees are found. As soon as a suitable place has been found ranchos or huts are built which are to be the *sarrapieros'* homes for perhaps two or three months. Once the fruit of the trees in the vicinity of the ranchos has been gathered, the men go farther into the forests, sometimes taking their supplies with them and remaining absent for a week or two.

The fruit of the tonka-bean tree resembles a mango in appearance, it has but little pulp which is sticky and tasteless, but edible. The seed (or bean) is covered with a hard furry substance. After a sufficient quantity of the fruit has been gathered

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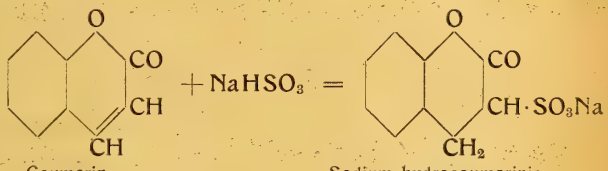
[1]) *Bulletin of the Pan-American Union; Americ. Perfumer* **10** (1916), 278. — [2]) According to A. Tschirch (*Handbuch der Pharmakognosie*, 2nd. vol., page 1310) English tonka beans, which are not handled in German commerce, are supposed to originate from *Coumarouna oppositifolia*, Aubl. (*Dipteryx oppositifolia*, Willd.). Seeds from *Dipteryx pteropus*, Mart. do not appear to come into the market, on the other hand the so-called wild or Brazilian tonka beans are said to originate from this species (Hartwich seems to think of a *Copaiba* species).

it is taken to some open place where it is further treated. The hard shell is carefully crushed between two stones and the single oblong seed removed and dried in the sun. These dried seeds are the tonka beans of commerce as they are sold to the merchants and exporters in Ciudad Bolivar. By the end of May or the beginning of June the crop is completed.

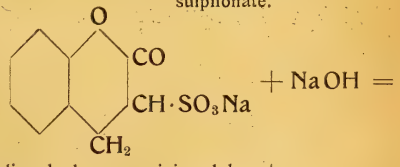
Before the beans are exported they go through a process of crystallizing by being steeped in strong rum or alcohol. Casks open at one end are filled with the beans to within about a foot from the top. The rum is then poured in until the cask is full when it is covered by layers of gunny bags. After 24 hours the rum not absorbed is run off and the beans are spread out to dry in a current of air. When first taken out the beans are of dark brown colour and are swollen with the absorbed fluid. On drying they shrink and become covered with coumarin crystals.

The price of the beans varies greatly. In 1912, the crop being small, the value rose to $ 4.87 per pound. The next year it fell to less than $ 1.— per pound. During the fiscal year ending on the 30th. of June, 1913, the United States imported 783888 pounds of tonka beans, valued at $ 1140409.—.

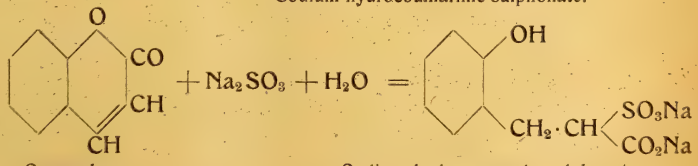
On the behaviour of coumarin with alkaline bisulphites nothing was known so far, with one exception, Rochleder having, many years ago, described a compound derived from æsculetin (a dihydroxycoumarin) a derivative which he considered an addition product of sodium bisulphite to æsculetin, but which at a later date was recognized by Liebermann as a sulphonic derivative of hydro-æsculetin[1]). Now F. D. Dodge[2]) has observed that coumarin and limettin (= citroptene, a dimethoxy-coumarin) readily yields well defined sulphonic derivatives. If coumarin is warmed on the water bath, with six parts of a 20 per cent. sodium bisulphite solution, with frequent shaking, a solution results which, on cooling, solidifies to a mass of crystals, readily soluble in water, $C_9H_6O_2 \cdot NaHSO_3 \cdot H_2O$, the sodium hydrocoumarinsulphonate. The salt may be titrated with accuracy, giving results which indicate the absorption of one molecule of alkaline hydroxide. When a concentrated solution of the compound is treated with caustic soda solution coumarin is precipitated which redissolves on continued agitation, but on further addition of alkali it is again separated. Finally coumarin ceases to separate and the liquid becomes permanently neutral. The explanation for this phenomenon is as follows: The crystalline sulphonate is a derivative of hydrocoumarin, containing the lactone ring intact. Alkali splits off the sulpho group, liberating coumarin which recombines with the neutral sulphite, forming the open-chain hydrocoumaric acid derivative about after the following manner: —



Coumarin. Sodium hydrocoumarinic sulphonate.



Sodium hydrocoumarinic sulphonate.



Coumarin. Sodium hydrocoumaric sulphonate.

[1]) See also *Berl. Berichte* 35 (1902), 2919. — [2]) *Journ. Americ. Chem. Soc.* 38 (1916), 446.

Coumarin, hence, should be soluble in neutral sulphite solution, which, in fact, is the case. The same neutral solution is formed as in the case of the titration of the hydrocoumarinic sulphonate. Potassium hydrocoumarinic sulphonate is obtained by warming coumarin with potassium bisulphite solution; it is less soluble than the sodium salt. The barium salt separates when a solution of barium acetate is added to a strong solution of the sodium salt.

Coumaric acid is formed by splitting off the sulpho group from the sodium salt of the hydrocoumarinic sulphonate. Dodge heats coumarin with a 25 per cent. sodium sulphite solution and evaporates to about half the volume; he then adds a 50 per cent. potassium hydroxide solution and evaporates to dryness on the water-bath. The yellowish green residue is dissolved in water and the cooled solution acidified with strong hydrochloric acid, when coumaric acid is precipitated. The yield is about 10 g. from 10 g. of coumarin.

Coumarin may be recovered from the hydrocoumaric sulphonate. For this purpose the sulphonate solution from 2 g. of coumarin was evaporated to dryness, pulverized and mixed with 5 cc. of acetic anhydride. On standing the mixture becomes solid by degrees and forms hydrocoumarinic sulphonate.

We have, then, here the following cycle of reactions: Coumarin $\rightleftarrows$ Hydrosulphonate $\rightleftarrows$ Hydrocoumaric sulphonate $\rightleftarrows$ Coumaric acid.

Recovery of coumarin from the hydrosulphonate presents some difficulty; decomposition with barium hydroxide gave the best results. The hydrosulphonate when heated at 130 to 160°, splits into coumarin, sodium sulphite, sulphur dioxide and water: —

$$2\,C_9H_7O_2NaSO_3 = 2\,C_9H_6O_2 + Na_2SO_3 + SO_2 + H_2O.$$

Limettin, also known as "citroptene", reacts with bisulphite solution when the sulphonate is formed, but the reaction takes more time than with coumarin. Attempts to prepare limettic acid were unsuccessful.

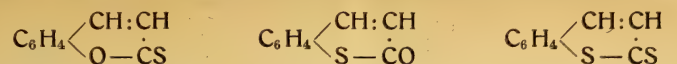
In conclusion Dodge deals with the hydrolysis of coumarin which he considers to be a suitable subject for a careful physico-chemical study.

Three sulphuretted analogues of coumarin are possible, according to whether in the molecule but one of the two atoms of oxygen has been replaced by sulphur (formula I and II), or both (III). The CS-thiocoumarin (thione-coumarin) has been known for some time and is readily prepared by the reaction of phosphorus pentasulphide on coumarin; unless purified by special method, it possesses an unpleasant, fecal-like odour. 1-Thiocoumarin (thiol-coumarin) (II) was prepared a few years ago by Chmelewsky and Friedländer[1]) from *o*-mercapto-cinnamic acid by intramolecular dehydration: $C_6H_4\langle^{SH}_{CH:CH\cdot CO_2H} \longrightarrow C_6H_4\langle^{S\cdot CO}_{CH:CH}$. This preparation does not possess the nasty smell of the thione-coumarin, on the contrary its odour is rather pleasant, resembling coumarin.

According to H. Simonis and A. Elias[2]) 1.2-dithiocoumarin (III) is obtained by heating 1-thiocoumarin with phosphorus pentasulphide; the product, when isolated from the reaction mass by boiling with benzene, cristallizes to beautiful deep red prisms and needles, m. p. 104°. Its fecal odour, which resembles that of 2-thiocoumarin, may be somewhat weakened by boiling with copper powder in benzene solution, but it cannot be made to disappear entirely. The mercurichloride compound melts at 237 to 239°, the aurichloride compound at 208 to 210°. 1-Thiocoumarin

[1]) *Berl. Berichte* **46** (1913), 1906. — [2]) *Berl. Berichte* **49** (1916), 763.

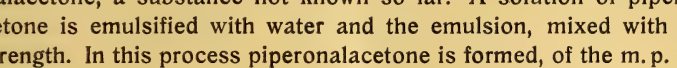
phenylhydrazone is formed by boiling the alcoholic solution of thiocoumarin and phenylhydrazine in the presence of copper powder and nitrate of lead; m. p. 140°.



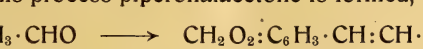
(I) CS-Thiocoumarin (Thione-coumarin). (II) 1-Thiocoumarin (Thiolcoumarin). (III) 1.2-Dithiocoumarin.

A monograph on coumarins published by Simonis will be found discussed on page 87 of this *Report*.

Heliotropin. In a paper by A. Kaufmann and R. Radosevic[1]) on the synthesis of *iso*quinoline derivatives we find particulars on the preparation of piperonylacetone from piperonalacetone, a substance not known so far. A solution of piperonal (heliotropin) in acetone is emulsified with water and the emulsion, mixed with soda lye of 40 per cent. strength. In this process piperonalacetone is formed, of the m. p. 107 to 108°.



Piperonal. Piperonalacetone.



Piperonylacetone.

By shaking a solution of piperonalacetone with hydrogen under ordinary pressure in the presence of colloidal palladium piperonylacetone is formed (m. p. 55°; b. p. 164 to 165° (12 mm)) which possesses a characteristic pleasant floral odour.

In the same manner methylvanillin yields 3.4-dimethoxybenzalacetone (m. p. 91 to 92°).

Menthol. R. Meldrum[2]) has published a few notes on the melting and solidifying point of menthol. Menthol becomes solid below its normal solidifying point because of its colloidal state which precedes crystallization. The solidifying point varies as also the colloidal state is variable, the variation amounting to 3.3° when using reliable methods. The melting point, however, is constant.

These observations are a further confirmation of our opinion expressed some time ago[3]) that the melting point is much more suitable for the evaluation of menthol than the solidifying point.

Musk. It is a well known fact that musk possesses an enormously strong and lasting odour. Nevertheless it is possible, as was found by C. B. Bazzoni[4]) to render musk odourless by exposing it for some length of time to a current of dry air. In an experimental way Bazzoni has proved this with an infinitesimally small quantity of musk. He allowed dry air to pass over a piece of musk weighing 1.32245 mg. for 7 months, checking the weight from time to time, when decreases of 0.00318 to 0.00002 mg. were observed. The musk had gradually become odourless and the odour did not return even if the musk was exposed to moist air. In order to determine these infinitesimal weights the author used a special micro-weighing balance of which he gives a short description.

That the odour of musk would disappear after some time was to be expected, for we have proved long ago that the odoriferous constituent of musk is volatilizable with

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[1]) *Berl. Berichte* **49** (1916), 675. — [2]) *Chem. News* **111** (1915), 229; *Chem. Zentralbl.* **1915**, II. 540. — [3]) *Report* April **1914**, 105. — [4]) J. Franklin Inst. **80** (1915), 463; *Journ. Chem. Soc.* **108** (1915), I. 1067.

water vapor. Some years ago we isolated from musk a volatile body, presumably a ketone of the composition $C_{15}H_{28}O$ or $C_{16}H_{30}O$, which we called muskone[1]).

Peru Balsam. One of the characteristic properties of Peru balsam is that, mixed with an even quantity of 90 per cent. alcohol, it gives a clear solution which, however, upon further addition of alcohol becomes turbid. This has been pointed out by the pharmaceutical press[2]) as well as by ourselves[3]) as complaints are made periodically by chemists as to indifferent solubility of the drug. It seems to be thought that it should be miscible in any proportion of alcohol. Such complaints are met with to this day.

To shew how important solubility on the lines pointed out above really is, is made clear by the examination of a sample on which we were called upon to pronounce our opinion early of this year. The properties were as follows: d_{15^0} 1.158, sap. v. 232.7, cinnamein content 62.4 per cent., ester v. of cinnamein 251.0; 1 g. was soluble in a mixture consisting of 3 g. chloralhydrate in 2 g. of water, also soluble in even vol. of 90 per cent. alcohol, and the solution, further diluted, also remained clear.

To judge from above figures the balsam answered all the requirements of a pure article and all the tests of the German Pharmacopœia. The only suspicious point was its comparatively weak odour and above all the fact that the alcoholic solution remained clear even when further diluted. It was just this deviation from the normal which induced us to examine the sample more closely, when it was found that the balsam was either heavily adulterated, or else that it was an artificial product altogether.

The verdict was based on the composition of the cinnamein. In the process of solidification a considerable difference was noticeable between this cinnamein and the same body obtained from pure Peru balsam. Whereas the latter solidified below zero, or at most very little above zero (we observed between $+1.5$ and -8^0), the cinnamein of the sample under examination had a solidification point of $+15^0$. If it is considered that benzyl benzoate solidifies at about $+18^0$, it follows that the cinnamein of the Peru balsam in question consisted almost exclusively of benzyl benzoate, a result which is contrary to experience on this matter. But besides, this cinnamein was found to contain chlorine from which it may be concluded with certainty that it was not a natural product, but that it contained artificial benzyl benzoate containing chlorine.

A further proof of the almost complete absence of cinnamic acid ester was produced in the following manner. We saponified the cinnamein, isolated the acids bound by the alkali and determined the cinnamic acid content of the acid mixture, after Liebermann's method[4]) as follows: About 0.2 g. of the acid mixture to be examined were dissolved in 10 cc. of 5 per cent. soda lye, diluted with 50 cc. of seminormal potassium permanganate solution and allowed to stand in a closed flask for two hours, with repeated shaking. Thereupon about 100 cc. of water were added, the whole filtered and washed again. The filtrate was acidulated with dilute sulphuric acid and the excess of potassium permanganate titrated back with seminormal oxalic acid at 70°. The quantity of cinnamic acid may be calculated from the amount of permanganate consumed.

$$3\,C_6H_5CH{:}CH\cdot COOH + 10\,KMnO_4 =$$
$$3\,C_6H_5COOK + 3\,K_2CO_3 + KHCO_3 + 2\,CO_2 + 4\,H_2O + 10\,MnO_2.$$

1580.3 g. of permanganate correspond with 444.18 g. cinnamic acid, consequently 1 cc. seminormal permanganate solution = 0.0044418 g. of cinnamic acid.

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[1]) H. Walbaum, *Journ. f. prakt. Chem.* II. **73** (1906), 488. — *Report* April **1906**, 94. — [2]) *Pharm. Zentralh.* **44** (1903), 241. — *Pharm. Ztg.* **48** (1903), 363, 754. — [3]) *Report* October **1909**, 139. — [4]) See H. Thoms, *Arch. d. Pharm.* **237** (1899), 280.

As was pointed out by Liebermann himself, this method is not absolutely correct, but it gives results which are exact enough for our purpose. With pure cinnamic acid, we found 96 per cent., with a mixture of equal parts of cinnamic acid and benzoic acid 47 per cent., and with a mixture of $^1/_3$ cinnamic acid and $^2/_3$ benzoic acid the result was 32 per cent. of cinnamic acid.

The acid mixture separated from the cinnamein under examination contained, as shewn by above-described test, 1.8 per cent. of cinnamic acid which confirmed our suspicion that the cinnamein consisted almost exclusively of benzyl benzoate. With five samples of cinnamein from pure Peru balsams, examined for comparison purposes, the cinnamic acid content varied, it is true, between 20 and 41 per cent., but the proportion of cinnamic acid to benzoic acid is, however, not to be compared with the cinnamein sample under examination.

To say the least of it, the balsam in question must therefore be looked upon as heavily adulterated, but possibly it was an artificial product, made, perhaps, in this way, that Peru balsam residues obtained in the manufacture of cinnamein were mixed with benzyl benzoate until the concoction shewed the constants of a pure balsam.

Safrole. J. Kläsi and O. Roth[1]) describe a case of safrole poisoning. The safrole, along with a number of other substances, possibly equally poisonous, was contained in a mixture which is said to be used under the name of Macassar oil as rubefacient in Java, and of which a certain quantity had been swallowed by accident. After ten minutes there were symptoms of unrest, vertigo, disturbed orientation, hallucinations, nausea, a powerful sensation of thirst and diarrhea. In the urine traces of albumen and urobiline were present, diazo-reaction producing a positive result. Among further symptoms there were paræsthesias, tonic spasms and temporary disapperance of the patellar reflexes. Mentally there were symptoms of desorientation, anxious disposition and delusions of hearing and sensation (feeling), also of sight and smell, furthermore delusions and divers katatonic symptoms (automatisms, echopraxia and verbigeration). This lasted for 17 days, after which the hallucinatory state gradually disappeared along with the anise-like odour of the expired air, until a few days later complete recovery set in. A remarkable fact were the strong variations in the intensity of the delirious symptoms, especially during the time the attention of the patient was attracted by incidents in his immediate proximity when all these symptoms disappeared and rational replies were elicited from the patient.

Styrax. Varying statements may be found in literature concerning the chemical composition of styrax balsam. Earlier authors assume the constituents to be isomeric alcohols, the storesinols of the formula $C_{35}H_{58}O_3$. Later research work by Tschirch and van Itallie appear to have solved the question definitely. According to their conviction the solid parts of storax balsam, the resin proper, consist of a single storesinol, bound to cinnamic acid, of the formula $C_{16}H_{26}O_2$, being isomeric with benzoresinol, a constituent of benzoin gum. M. Henze[2]) now makes the surprising communication that this resin contains considerable quantities of free pimaric and abietinic acids which, so far had been considered exclusively as characteristics of the resins of conifers, but it is now shewn that also deciduous trees form this acid[3]). On the other hand it must not be lost sight of that the resins from conifers are pathological products

[1]) *Monatsschr. f. Psych.* **38** (1915), 235; *Therap. Monatsh.* **29** (1915), 687. — [2]) *Berl. Berichte* **49** (1916), 1622. — [3]) Styrax balsam originates from *Liquidambar orientale*, Mill. (N. O. *Hamamelidaceæ*).

which appear only as the result of a deep artificial lesion of the tree. The same may be said of styrax, for normally no flow of gum may be seen in the styrax tree. As regards formation styrax and turpentine are therefore identical. Thus it might well be possible that the characteristic acids are formed by one and the same, or another, closely related mother-substance and it is not impossible that they are more widely spread than was presumed so far.

In this connection it is interesting to note that the so-called peripherous resin of certain conifers, a term used for the resin or gum which exudes spontaneously from the tree, and which is therefore a physiological secretion, has a different chemical composition.

To eliminate the acids, styrax is dissolved in 70 to 80 per cent. alcohol on the water-bath and kept in the cold over night. A dark oil will be found separated at the bottom of the vessel. The supernatent clear dark-yellow, alcoholic solution is next precipitated with an alcoholic neutral acetate of lead solution. On heating the strong precipitate is dissolved again almost completely in the precipitation liquid and on cooling it separates in crystalline form. This solubility is due to the esters and terpenes contained in styrax. In pure alcohol the acetate of lead deposit is practically insoluble. The original solution may also be precipitated hot, in which case a crystalline deposit is obtained at once on cooling. The safest way quickly to obtain crystalline products is to dry the precipitate thoroughly whereupon it dissolves almost completely in chloroform. From chloroform, or, better still, from a mixture of chloroform and acetic ester it may be recrystallized. The lead salt thus obtained is dissolved in glacial acetic acid with a slight addition of alcohol and is poured slowly into a sufficiency of water, strongly stirring the while. A flocculent, pure white substance is separated which coagulates on warming and becomes quite hard and brittle upon cooling. By repeated recrystallization from a mixture of glacial acetic acid with acetone or methyl alcohol and finally from methyl alcohol alone crystals of the m. p. 140 to 150° are obtained. By purification with the sodium salt the author succeeded in preparing from these crystals an acid of the m. p. 210 to 211° which proved to be identical with *d*-pimaric acid. The second substance forming the bulk of the original acid mixture crystallizes from dilute methyl alcohol and melts at 158 to 165°; α_D — 39° 36′. Indications in literature on the melting point of abietinic acid vary considerably, more especially so in earlier publications. In the author's opinion the acid of the m. p. 158 to 165° appears to be identical with abietinic acid. Its behaviour when heated, in which process it develops carbonic acid and forms butyric acid, points to abietinic acid.

Thymol. A "highly important" piece of news, from which it is palpable that the German chemical industry is now finally and completely beaten, comes from England[1]). The firm of Rubeck — a thoroughly English-sounding name, to be sure — which had mastered the terribly difficult task of producing thymol crystals already last year (even though their quality did not, by any means, come up to the requirements of the British Pharmacopœia)[2]), has prepared thymol crystals from thyme oil, the crystals being of particularly colossal dimensions that a show-piece weighing 650 g. was reproduced in the form of an outline picture, needless to say with the required amount of tom-tom beating. Unfortunately, said picture does not convey the impression of a beautifully formed crystal at all, but rather of an irregular crystalline mass. In how far the imperfection of the reproduction is at fault we cannot judge, but for the benefit of

[1]) *Chemist and Druggist* **88** (1916), 676. — [2]) See *Report* October **1915**, 54.

those who should not be aware of the fact we may mention that in judging thymol the size of crystals counts for nothing at all, but only the purity of the preparation, in this case the melting point. On this point, however, the paragraph in question is absolutely silent.

Manufacture of thymol is said to have been attempted successfully in India too, evidently from ajowan oil, and, as far as we can gather from the reports to-hand, on a small scale only[1]). The "Technical Laboratory of the Department of Industries, United Provinces of India" advocates by circular the manufacture of thymol in India, where the raw material is cheap and where very good samples were produced by experiments carried out in the laboratory. The circular continues:

"Thymol was sold before the war at 5 to 6 shillings per lb. The price jumped up enormously soon after the supplies from Germany were stopped, and not so long ago thymol was quoted at 30 shillings per pound. It is obvious that the manufacture of thymol in India at the present time should yield a good return. Even under normal conditions there is no reason why thymol should not be made in India at least as cheaply as elsewhere, seeing that we have the raw material in our midst, and a small company has recently been established in Dehra Dun for its manufacture. The apparatus required is simple and inexpensive. The demand for thymol both in India and in Great Britain is great, and there should be no difficulty therefore in finding a ready sale".

According to R. Meldrum[2]) the point of solidification of thymol varies between 48.2 and 49.2°. The variation depends on the width of the test tube and the absorption of moisture by thymol. The higher value must be looked upon as being more correct as it approaches the melting point more closely.

On a previous occasion[3]) we felt called upon to state that we consider it more correct if in the evaluation of thymol the melting point, and not the solidifying point, is considered as there can be no doubt but that the former can be determined more exactly. The observations made by Meldrum only confirm our opinion.

Althoff[4]) reports on the use of thymol in cases of *Herpes zoster*. He considers this complaint an accute infection requiring a corresponding treatment and he recommends the following ointment: —

Rp. Thymoli	1.0
Acid. carbolic. liquefact.	1.0
Vaselin. albi	ad 100.0

This ointment is placed twice a day on the affected part. Moreover three times a day a powder is given consisting of 0.5 g. urotropine and 0.5 g. aspirine in half a glass of water, followed by a cup of hot tea. Treatment should be started as early as possible: it relieves the pain and the itching and shortens the duration of the complaint.

According to A. Géronne and W. Lenz[5]) another practical use for thymol consists in treating typhoid bacilli carriers with thymolized charcoal. Their experiments were dictated by the intention to use the coal as carrying medium for the desinfectant and in this way to avoid too quick an absorption of the remedy. In three obstinate cases,

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[1]) *Daily Consular and Trade Reports*, Washington, N° 37 of February 14th. 1916, page 610. — [2]) *Chem. News* **111** (1915), 193; *Chem. Zentralbl.* **1915**, II. 536. — [3]) *Report* April **1914**, 105. — [4]) *Münch. med. Wochenschr.* **1914**, 1916; *Merck's Jahresber.* **28** (1914), 457. — [5]) *Berl. klin. Wochenschr.* **52** (1915), 341; *Chem. Ztg. Repert.* **40** (1916), 27.

where the patients kept throwing off bacilli, 3 g. of charcoal and 3 g. of thymol were given daily in single doses of 1 g. of each, the charcoal half an hour before, the thymol half an hour after meals. Treatment lasted from 8 to 14 days during which time no appreciable incommodation of the stomach could be observed. In all three cases the secretions became free from typhoid bacilli after the time above mentioned. The charcoal used was dry finely powdered animal charcoal from Merck's. In every instance bacteriological examination of the fæces showed an appreciable alteration of the picture on the Endo-plate. It is evident that in this respect thymol as well as charcoal are useful, but more especially so in combination.

According to a communication of the Agricultural Department of the United States[1]) it would pay, given favourable conditions, to cultivate the labiate *Monarda punctata*, L., known there by the name of horsemint. Many years ago the Department undertook cultivation experiments in this respect with this plant which grows wild on light sandy soils and may be found all over the district bordered by Southern New York, Florida, Wisconsin, Kansas, and Texas. Wherever it grows wild it is to be expected that it will flourish in the cultivated state as well. Whether cultivation will pay will depend on local conditions. In the distillation of the plants an average yield of about 20 lbs. of oil per acre may be expected; in subsequent years the yield should amount to at least 30 lbs. per acre. The oil contains about 70 per cent. of phenols, chiefly thymol[2]). Consequently an acre should yield about 13 lbs. of thymol the first year and about 20 lbs. in subsequent years. A Monarda plantation will stand five years and more; but cultivation would only pay if at the same time other aromatic plants were cultivated, thus making it worth while to invest in a distilling plant.

Vanillin. The titration method in the examination of vanillin, proposed by J. F. Sacher[3]) is attacked by M. Lehmann[4]) who points out that it is incorrect to assume that all the vanillins of commerce are one and the same homogenous body. Very often one has to deal with a mixture of isomerides and for such products Sacher's titration method would invariably find 100 per cent. of pure vanillin. The presence of by-products of the same molecular weight, and behaving in exactly the same way to alkalis, is not detected by Sacher's method. Lehmann also holds it to be possible that additions of salicylic, benzoic or phthalic acids could be graduated by means of a second addition, indifferent to alkalis, so that titration with alkali would yield apparently 100 per cent. of vanillin. In a mixture of 61 g. of benzoic acid with 76 g. of vanillin and 15 g. of acetanilide, which mixture consequently contained but 50 per cent. of vanillin and 50 per cent. of adulterants, Sacher would find 100 per cent. of pure vanillin according to his method. Finally Lehmann points to an error of calculation in Sacher's paper. Sacher admits the error, but points out in his reply[5]) that an isomeride such as *f. i. iso*vanillin, would be out of the question as an adulterant because of its being too expensive, and that it was but a technical impurity. Furthermore he critisizes Lehmann's method of determining the melting point which he declares to be inexact and he maintains the reliability of his own method.

We mentioned already in our last *Report*[6]) that in putting Sacher's method to the test, we obtained indifferent results only.

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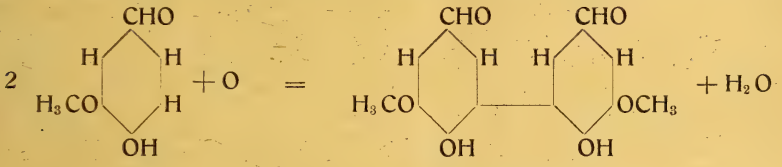
[1]) *Bulletin* 372; *Americ. Journ. Pharm.* 88 (1916), 287. — [2]) See Gildemeister und Hoffmann, *Die ätherischen Öle*, 2nd. ed., vol. III, page 494. — [3]) *Deutsche Parf.-Ztg.* 1 (1915), 187; *Report* October **1915**, 54. — [4]) *Deutsche Parf.-Ztg.* 1 (1915), 288. — [5]) *Deutsche Parf.-Ztg.* 1 (1915), 289. — [6]) *Report* October **1915**, 54.

As far back as 1893 K. Elbs[1]) had found that direct hydroxylation of the benzene nucleus was possible by means of oxidation with persulphates; in this manner he prepared nitroquinol from *o*-nitrophenol, and soon after a few patents were taken out for the analogous preparation of quinol derivatives from phenols with free *para*-position as well as pyrocatechine from phenols with occupied *para*-position.

On the behaviour of hydroxyaldehydes with persulphates there have so far been but a few communications by Neubauer and Flatow[2]) who obtained much in the same way gentisine aldehyde, $C_6H_3(OH)_2(CHO)$ from salicylaldehyde, $C_6H_4(OH)(CHO)$. When extending the persulphate reaction on anisaldehyde, piperonal, and vanilline, K. Elbs and H. Lerch[3]) ascertained that no hydroxylation of the benzene nucleus takes place. Anisaldehyde produces a nearly quantitative yield of anisic acid, whilst with vanillin and piperonal oxidation sets in in the benzene nucleus along with condensation and formation of diphenyl derivatives, vanillin being converted to dehydrodivanillin[4]).

In the process of oxidation of vanillin the peculiar phenomenon is observed that the yield depends in a large measure on the kind of the persulphate used. The sodium salt gives a quantitative yield of dehydrodivanillin, the potassium salt 60 to 70 per cent.



Vanillin. Dehydrodivanillin.

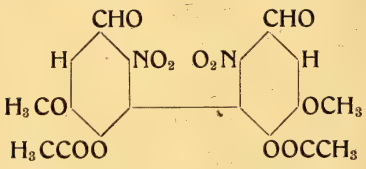
and the ammonium salt 50 per cent. only of the calculated quantity. Tiemann had used at the time ferric chloride for the oxidation of vanillin, a process which produced, even though in small yield, a dehydrodivanillin of great purity, whilst the preparation produced by means of persulphate becomes mixed with impurities which are very difficult to eliminate. If, however, ferrous sulphate is used as oxygenator a pure dehydrodivanillin is obtained also by means of persulphate.

In the preparation of dehydrodivanillin the authors proceed as follows: — 30 g. vanillin are dissolved in 2 litres of water on the water-bath, and while stirring the solution first 1 g. of ferrous sulphate and thereafter 25 g. of sodium persulphate are added; after 30 minutes the liquid is drawn off, the precipitate dissolved in dilute potash lye and precipitated with dilute hydrochloric acid. In this way 29 g. of chemically pure dehydrodivanillin of the m. p. 305° are obtained. The position of the diphenyl bond in dehydrodivanillin, which had not been established so far, has been ascertained by the authors by an examination of the nitroderivatives. Of course nitration offers difficulties and also the nitration of the dimethylether and the diacetyl compound requires strictest observation of definite experimental conditions. The dimethylether is nitrated to dinitrodehydrodivanillin dimethylether by treatment with fuming nitric acid and concentrated sulphuric acid. In exactly the same way diacetyldehydrodivanillin yields dinitrodiacetyldehydrodivanillin (I) (m. p. 90°) which, by reduction with tin and hydrochloric acid, is converted to diacetyldimethoxydehydrodianthranil (II). As by the formation of the dianthranil derivative the *ortho*-position of the nitro group to the aldehyde groups is proved, the position of the diphenyl bond is determined. For besides the suggested formula for the dinitrodiacetyldehydrodivanillin only one more (III) would remain in

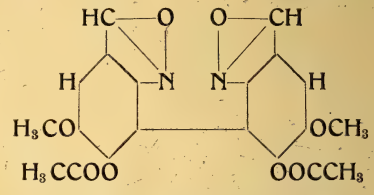
[1]) *Journ. f. prakt. Chem.* II. **48** (1893), 193. — [2]) *Chem. Zentralbl.* **1907**, II. 901. — [3]) *Journ. f. prakt. Chem.* II. **93** (1916), 1. — [4]) F. Tiemann, *Berl. Berichte* **18** (1885), 3493.

which the aldehyde groups would find themselves in *ortho*-position to the diphenyl link, a proposition which is untenable. For it is contrary to all experience that an additional substituent, in this case the nitro group, would take up a *meta*-position to an acetylated phenol group as long as an *ortho*-position is vacant, and at the same time an *ortho*-position to an aldehyde group, as long as a *meta*-position is available for it.

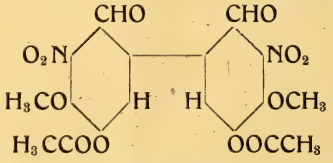
Of derivatives of dehydrodivanillin the authors furthermore produced dehydrodivanillin dimethylether which, according to Tiemann, is obtained by the action of methyl iodide on the sodium salt of dehydrodivanillin; m. p. 136°; diphenylhydrazone, m. p. 234°. By heating dehydrodivanillin with acetic anhydride diacetyldehydrodivanillin (m. p. 117°) is formed which is oxidized to diacetyldehydrodivanillic acid by permanganate of potash. Tiemann has found that dehydrodivanillic acid cannot be prepared by direct oxidation of dehydrodivanillin, but it is easily obtained by saponification of diacetyldehydrodivanillic acid; it melts at 295°. As a by-product in the process of oxidation of diacetyldehydrodivanillin, diacetyldehydrovanillindiacrylic acid methylketone (diacetonyldiacetyldehydrodivanillin) is formed, which may become the main product if no excess of permanganate is used; m. p. 246°.



(I) Dinitrodiacetyldehydrodivanillin.



(II) Diacetyldimethoxydehydrodianthranil.



(III) Formula for dinitrodiacetyldehydrodivanillin, untenable from theoretical reasons.

The three species of vanilla cultivated in Tahiti have been examined botanically by Constantin and Bois[1]). These are: Mexican, Tahiti, and Tiarei vanilla. Mexican vanilla originates from *Vanilla planifolia,* Andrews, Tahiti vanilla, which is the most usually cultivated kind in the island, of a variety of *Vanilla planifolia* for which the authors propose the name of *angusta;* the third species has made its appearance in the island about six years ago. It has not been possible so far to ascertain where it comes from. The fruit is very large (up to 10 inches) and possesses a pleasant and mild, though weak, flavour. Its commercial value (fr. 25.— per kilo in July 1914) is greater than that of the Tahiti vanilla. Constantin and Bois have called this kind *Vanilla Tiarei.*

On page 93 of this *Report* we have dealt with a colorimetric method of determining vanillin in vanilla.

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[1]) *Compt. rend.* **161** (1915), 196.

Notes on Scientific Research in the Domain of the Terpenes and Essential Oils.

General.

Prospects for the cultivation of aromatic plants in Asia minor.

Given the keen interest, which in consequence of the war is shown to the Orient, and taking into consideration the great importance which especially Asia minor will surely have for us in future, it is worth knowing what districts of it are suitable for the cultivation of aromatic plants. According to K. Krause[1]) there are three climatic provinces, the outline of which is so pronounced as it is possible only in the temperate zones. On the North coast, there are moist, mild winters; in the interior, the climate is distinctly continental; and in the Western part of the peninsula, which comprises the mountainous slope of the highland towards the Mediterranean and the greater part of the South coast, the climate is pronouncedly mediterranean. Apart from the border zone, which generally occupies a narrow space only, there predominate in the lower, hotter and drier sites those evergreen, dense shrubs, which are characteristic for all mediterranean countries and are mostly named *"Macchie"*. They, as well as the carpets of low, herbaceous plants occurring between them, are extraordinarily rich in odorific substances. Their region is the only one that might come into consideration for the cultivation of aromatic plants.

Pharmacogeographical notes on essential oils and drugs.

Numerous indications concerning products which are important for us are to be found in a treatise by H. Zörnig, entitled "notes on pharmacogeography"[2]). In order to obtain highly reliable information, with due regard to the local conditions of the districts concerned, on export, statistics, traffic, cultivation, &c., he applied to a considerable number of export firms abroad and to all the German Consulates. In addition, he availed himself of the official statistics of the German Empire as well as of foreign countries, of private communications and of the latest literature in the domain of scientific journeys, applied botany and geography, but intentionally made little use of older works, as, no doubt, certain changes have taken place in the last fifty years.

In Abyssinia, three regions are to be distinguished according to altitude; *viz.*, the *"Kolla"* (up to 1700 m.), the *"Woina-Deka"* (up to about 2600 m.) and the *"Deka"* (from and above 2600 m.). Fennel-flower-seed *(Asmuth,* from *Nigella sativa,* L., N. O. *Ranunculaceæ)* is grown in the *"Kolla"* and *"Woina-Deka"*, Korarima cardamoms only in the *"Kolla"* and coriander in the *"Woina-Deka"*. In 1913, 1200 kilos of Korarima cardamoms were exported to Germany. Mustard (*Senafitsch,* from various *Sinapis* and *Lepidium* species) is worked by the aborigines themselves. Abyssinia is the chief exporting country for

[1]) *Deutsche Parf.-Ztg.* **2** (1916), 241. — [2]) *Arch. der Pharm.* **254** (1916), 149.

civet (in Arabic and Abyssinian *„Sebbat"*), its share being about $^6/_7$ of the total production, whereas only small quantities come from Nubia. Civet is obtained principally in the southwestern provinces, in Gera, Kaffa, Wollaga, Limmu and the adjoining Galla districts, where the wild valleys with their woods favour the occurrence of the civet cats. These are caught, kept in narrow cages and reared exclusively by aborigines. The product is collected in Addis-Abeba and exported via Djibouti. The quantity exported is estimated at from 500 to 600 kilos yearly. The larger part goes to the Orient, especially to Arabia, Turkey, Egypt and India, the smaller part to France. Of late small quantities have been sent direct to Germany[1]), *f. i.* 12 kilos in 1913.

Eritrea exports civet as an Abyssinian product.

Egypt exports coriander and cumin seeds, and apricot kernels go to Germany for the production of fatty oil. Frankincense (from *Boswellia papyrifera,* Rich., N. O. *Burseraceæ,* in Arabic *Gafal*) comes from Sennar and goes via Alexandria to Europe or via Aden to India, wherefrom it is re-exported. A product very similar to frankincense is supplied by *Daniella thurifera,* Bennett (N. O. *Leguminosæ*)[2]) in Bahr-el-Gazal and by *Commiphora pedunculata,* Engl. (N. O. *Burseraceæ,* in Arabic *Luban*). The African Bdellium comes from *Commiphora africana,* Engl., in Sennar and Cordofan, and Mecca balsam is obtained from *Commiphora opobalsamum,* Engl. As said before, Nubia exports some civet, 42 kilos of which reached Germany in 1913.

Tripoli exports caraway (cumin?) and fennel seeds in large quantities, but nothing exact was to be found out with regard to the exports of apricot kernels and almonds, which, however, are very inconsiderable in any case.

Tunis exports oil of neroli and orange-flower water. Both products are obtained exclusively in the neighbourhood of Nabeul, the annual output being about 74000 to 85000 quarts of the latter and 200 lbs. of the former from approximately 200000 lbs. of orange-flowers (*Citrus Aurantium,* L., *subspec. amara,* L.). These articles are almost entirely taken up by France. As regards spices, laurel leaves, sage *(Salvia officinalis,* L., N. O. *Labiatæ),* coriander and caraway seeds come into consideration. In 1913, Germany imported from Tunis 1400 kilos of coriander, caraway, &c., and 5200 kilos of laurel leaves, sage, &c.

In Algiers, there are the chief geranium growing districts Staouéli, the Metidja plain and Boufarik, altogether more than 500 ha., the trading centre being Boufarik, about 35 km. to the West from Algier. The quantities exported varied from 25000 kilos in 1912 to 53600 kilos in 1904, being on an average 40700 kilos annually for the years from 1901 to 1912[3]). The average value is estimated at 900000 Francs yearly. Eucalyptus oil was exported to the extent of 11400 kilos in 1912 or 21500 kilos on an average for the period from 1901 to 1912. The plantations of the camphor tree are still inconsiderable. In 1913 the exports to Germany of essential oils produced in Algiers amounted to 4200 kilos. *Ferula communis,* L. *(*N. O. *Umbelliferæ),* occurring frequently near the border of Morocco, yields a resin very similar to ammoniacum, and which is said to be identical with the African ammoniacum, formerly exported from Fasoy in Morocco.

Morocco exported in 1913 to Germany 11400 kilos of Ginger. The export figures for caraway and coriander were 553000 and 563000 Francs, respectively, in 1911, whereas there were none available for cumin. Almonds were exported to the value of 5568000 Francs in 1911, and in 1913 there were 2100000 kilos sent to Hamburg.

[1]) It goes without saying that Germany requires far more, but imports of this article used to come via France. [2]) See *Report* April **1911**, 145. [3]) See *Report* April **1914**, 64.

For South Morocco alone the annual crop is estimated at 1500 tons. As to apricot kernels, about 36 000 kilos reached Hamburg in 1909.

Sierra Leone grows and exports cubebs (from *Piper Cubeba*, L.) and, in 1912 exported 2200 tons of ginger, worth 44 863 £, almost entirely to Great Britain. No export figures could be obtained for Melegueta pepper.

Liberia sent 7200 kilos of ginger to Germany, in 1908.

"How to secure the manufacture of synthetic aromatics by the French industry" is the title of a lecture, given on April 24th. 1915 at a public meeting of the *"Société d'Encouragement pour l'industrie nationale"*, by J. Dupont[1]). He is of opinion that the French industry will succeed in future to cover France's requirements of artificial aromatics. He strongly opposes the assertion found in the French press since, and even before the beginning of the war, that synthetic perfumes forcedly belong to the products styled "German rubbish" *(camelote allemande)* and calls attention to the fact that not everyone of them is of German invention and that they are not at all necessarily crude and common goods. He even holds that the introduction of synthetics contributed to the social progress, fostering a tremendous increase in the use of perfumes through making these luxuries, formerly reserved to the "upper ten", accessible to the lower classes. Owing to the chemical aromatics, the perfumer is in a position to offer cheaper articles and to secure a wider range of customers. The consumption of natural perfumes increases at the same rate, for the synthetics do not usurp the place of the natural products but combine with them in order to obtain greater strength or to form new compositions.

After a survey of the countries using synthetics, in which he states that they all depend upon German, French, Swiss and Dutch factories[2]), he deals with the situation in France. The first question is, What share has France in the manufacture of synthetics? It is easy to establish the quantities imported, for there is a special number for them in the customs tariff. The imports came up to the following values: —

Frs.	1 424 000.—	in	1912,
„	1 429 000.—	„	1913,
„	742 000.—	„	1914,

whereas the exports given as

Frs.	192 000.—	in	1912,
„	165 000.—	„	1913,
„	373 000.—	„	1914

must be far from exact, as he thinks that even the most modest among the French factories exports more than the totals given. According to his opinion, the fault lies with the exporters, who scarcely ever declare "synthetic aromatics" but use more general terms. Dupont holds that those concerned ought to cease with this practice, as being detrimental to themselves, for the importance of this branch of industry is thus, in an official document, lowered in the eyes of foreigners. Another important source of mistakes arises, he states, from the fact that post parcels only appear in bulk in the statistics[3]).

French manufacturers had often been reproached with their disinclination to travel, their incapacity to understand the wants of their customers and their unwillingness to

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[1]) *Bull. Sciences pharmacol.* **22** (1915), 278. — [2]) He indicates the number of factories as 12 for Germany, 8 for France, 4 for Switzerland, and 2 for Holland. — [3]) Presumably because the contents of the parcels are not indicated in the statistics.

take them into consideration. According to Dupont, French manufacturers of synthetic aromatics do not deserve a similar reproof and have nothing to learn from other countries with regard to the organisation of their trade.

As to the manufacture of synthetics in France, only benzaldehyde and benzyl acetate could not be made so far. The reason was obvious, benzaldehyde being the raw material for the production of dyes and its manufacture monopolized by the mighty German works, the same holding good of late for benzyl acetate. With regard to other aromatics, France was in a much better position, which would be strengthened as the general conditions improved for the chemical industry. The French industry ought to free itself from its dependence on Germany, for the danger of which the lecturer gives some instances[1]). According to Dupont, the raw material (coal tar) and the water power available are sufficient, nor are knowledge and money lacking. It would only be required to work hard and to persist, paying attention not alone to the products which bring great profits but also to the less remunerative ones.

He then discusses the question concerning workmen and chemists and comes to the conclusion that the careful, intelligent and clever French workman adapts himself marvellously well to such a sensitive industry and that it is astonishing with what ease he carries out the most delicate operations of organic chemistry. If they were only given the necessary theoretic knowledge, through special courses of lectures in the factories themselves, they could even be made into the badly wanted higher grade employees. Chemists were supplied by the *École de Physique et de Chimie industrielles* of Paris, the Institutes for Applied Chemistry of Paris and Nancy, as well as by the Lille, Lyons, Rouen and Toulouse schools, so that in this respect France would not be behindhand at all.

However, as regards the outfit of the factories for making laboratory and other apparatus from lead, aluminium, porcelain, enamelled iron, &c., suction- and vacuum-pumps as well as filtering presses, France would still have to work very hard, a satisfactory result being obtainable only by a close collaboration of the builders of such apparatus with the manufacturers whom they are to supply.

As other important questions he mentions the customs and the patents law and the alcohol question.

Dupont thinks that it is not correct to attribute the comparatively low level of the French industry, as is sometimes done, to the disadvantages connected with the fiscal laws concerning the use of alcohol in certain branches of manufacture. He distinguishes between two kinds of use of alcohol; *viz.*, in reactions and as a medium for crystallization. In the former case, the French manufacturers would not be handicapped in comparison with their foreign competitors, apart from the high price of the alcohol, whereas the matter would be different in the latter. Alcohol is the only suitable medium for crystallizing heliotropin, coumarin and artificial musk, and the French authorities had permanently refused to take the view of those in Germany and Switzerland, according to which such alcohol is to be considered as denatured. They had at least exercised a continuous supervision, causing considerable costs and inconvenience to the manufacturers. Said unwillingness to take another point of view in the matter might be founded in the duties with with the alcohol used for crystallization was charged in the products imported. These duties differed, however, for every product, the calculation was rather intricate and the consequence was that the

[1]) He mentions the want of raw materials, especially benzyl chloride, cresoles, potash and magnesium, through which several French works are crippled at present.

French manufacturers were handicapped in the export of their goods, as their foreign competitors did not have to pay such duties. The French perfumers must therefore pay coumarin, heliotropin, terpineol and vanillin much higher than their foreign competitors. It was easy to understand that the French industrials would like to find a practical way how to discharge the alcohol used for crystallization of taxes for consumption.

The duties on imported raw materials were moderate, generally speaking, and some of these were altogether free from them, such as the direct derivatives of coal tar and some essential oils.

Regarding the manufacture of terpineol from oil of turpentine, the French industrials were under a disadvantage, owing to the duty on the latter.

Oil of cloves, an important raw material for the industry of the aromatics, had not been made in France so far, although facilities had been granted by the authorities, the distillers not having to pay the high duty on cloves, if they deliver 15 kos. of the oil for every 100 kos. of cloves (the oil pays a duty of ½ Franc per ko., if consumed in the country, whereas it may be exported free of charge). In Germany, England and Holland, however, the distillation of cloves was flourishing.

The production of essential oils in France is, a well-known fact, localized at Grasse, which is without any competition, as far as the flowers growing there were concerned, whereas it is not so well placed as England and Germany with regard to the distillation of foreign produce. The fuel question alone would be sufficient as an explanation, the costs of conveyence from Marseilles to Grasse being fairly high. Dupont holds that the distillation of essential oils can only be carried out successfully in the port, where the raw material is discharged, provided that there are coal mines in the neighbourhood. The best solution of the duty question would be that there was a free port for the purpose, the creation of which might perhaps be a consequence of the war.

Dupont considers as a considerable protection for the French industry the fact that the synthetic aromatics have been brought under a special tariff; a double-edged sword, however, as it protects the manufacturers of such articles, but is detrimental to the interests of the perfumers, who are exporters above all, if they are bound to buy certain materials abroad. It would, therefore, be necessary that the manufacturers of synthetics redoubled their efforts in order to supply the perfumers with everything required, so that there was no danger any more for them to become dependent again on present enemies, in however small a degree it might be.

In Dupont's opinion, the patents question is complicated and difficult, for, generally speaking, inventors in the domain of synthetic aromatics did not have their discoveries patented, as it was difficult to prove any breach of patent in this special branch of industry, in which very often articles were concerned that might be made privately on a small scale and secretly sold. As the French law gave the inventor the absolute right of property for 15 years, better methods of production, discovered in the meantime and which, by working out cheaper, would increase the consumption, could not be worked. A good many people (Dupont among them) think that this system creates an abusive privilege in favour of a few and injures the general interests, as it brings about a standstill in that the owner of the patent has no incitement to produce anything better and nobody else will trouble to find out better methods without any chance to apply them. This might, perhaps, be one of the reasons for the backwardness of the French industry. Dupont mentions, besides, that the question of a preliminary examination of patents has roused the interest of specialists.

Following up this lecture, we reproduce a short note on the conditions of the French industry of synthetic aromatics in the beginning of the present year[1]). During the first months of the war, the stocks were consumed and prices remained stationary. A few months later, a tremendous rise set in, due only in part to the absence of the German products, which had been plentiful and cheap before the war, but chiefly to the calling under arms of the technical staff. In addition, nearly all the raw materials were commandeered by the Government, an overzealous measure, with the effect that the few factories of synthetic aromatics which were in a position to continue working with overaged or disabled people were forced to import at great cost from the United States small quantities of certain products, otherwise made much cheaper by themselves, if only the Government had shown a slight desire to meet them.

Statistical notes on the perfume industry in the South of France.

The report of the Nice Chamber of Commerce for the year 1914[2]) gives some details regarding the importance of the Perfume industry in the Maritime Alps. It says *e. g.*, "There are 70 works in Grasse, Cannes, Le Cannet, Golfe-Juan, Vallauris, Nice, and Antibes which participate in this branch of industry, the centre being Grasse, where at least half of these factories are situated. The total staff is estimated at from 2300 to 2400, workers and clerks, among whom there are many women. Two-thirds of the workers are Italians. The yearly turnover amounts to about 6 000 000 $, in which the share of Grasse is at least 4 000 000 $[3]). More than two-thirds of the total are due to exports.

The trade in raw materials for the perfume industry might be more extensive, but Germany and Switzerland are serious competitors with their artificial aromatics, the use of which goes on taking greater proportions".

In an article dealing with the trade and the industry of the Seychelles[4]), we find the following export figures: —

	1913	1913	1914	1914
Cinnamon bark	13 962 cwts.	53 305 Rs.	11 805 cwts.	44 649 Rs.
Vanilla beans .	120 „	101 847 „	210 „	131 730 „
Essential oils .	924 gals.	16 482 „	1 870 gals.	35 325 „

The vanilla beans were destined chiefly to Great Britain, the cinnamon bark to Germany, Holland, Great Britain, and Austria, the essential oils to Germany, Great Britain, and France.

Bibliography.

In April last, the third volume of the second edition by E. Gildemeister of *"Die ätherischen Öle"* by Gildemeister and Hoffmann made its appearance, so that the work is now complete (price: ℳ 17.— per volume in paste, or ℳ 20.— if bound; published by Schimmel & Co.; for booksellers: L. Staackmann, Leipzig). The volume before us deals with the oils of *Rutaceæ* (continuation of the second volume), *Burseraceæ, Meliaceæ, Polygalaceæ, Euphorbiaceæ, Anacardiaceæ, Aquifoliaceæ, Celastraceæ, Sapindaceæ, Vitaceæ, Gonystilaceæ, Tiliaceæ, Malvaceæ, Sterculiaceæ, Theaceæ, Guttiferæ, Dipterocarpaceæ, Cistaceæ,*

[1]) *Parfum. moderne; Perfum. Record* 7 (1916), 6. — [2]) *Americ. Perfumer* 10 (1916), 304. — [3]) If these figures are correct, the importance of Grasse has hitherto been overrated. — [4]) *Bull. Imp. Inst.* 13 (1916), 468.

Winteranaceæ (Canellaceæ), Violaceæ, Turneraceæ, Caricaceæ, Thymelaceæ, Lythraceæ, Myrtaceæ, Araliaceæ, Umbelliferæ, Pirolaceæ, Ericaceæ, Primulaceæ, Oleaceæ, Gentianaceæ, Apocynaceæ, Asclepiadaceæ, Convolvulaceæ, Verbenaceæ, Labiatæ, Solanaceæ, Scrophulariaceæ, Acanthaceæ, Rubiaceæ, Caprifoliaceæ, Valerianaceæ and *Compositæ* as well as with some of unknown botanical origin. Besides, there are several additions, an index of the plants yielding essential oils, classified according to the N. O., and a general index. The volume contains 51 illustrations in the text, 5 maps and a table of curves. The number of essential oils dealt with has risen in the second edition from 422 to 952.

As the 8th. volume of the collection *"Chemie in Einzeldarstellungen"*, edited by Prof. Dr. Julius Schmidt, a monography of the coumarins has been written by H. Simonis[1]), in which the author has compiled everything written on these bodies up to the end of 1915. It is self-evident that principally coumarin derivatives are dealt with which are of little or no interest for our special domain, but the coumarin itself, so important for our industry, is discussed in detail too. Many interesting particulars referring to the history of coumarin are given. It was discovered by Vogel, in 1820, in the Tonka beans, the seeds of *Dypteryx odorata* or *"coumarouna"*. In the beginning, it is true, it was taken for benzoic acid, until Guibourt and later on Boullay and Boutron-Charlard (1825) recognized the peculiarities of the "Tonka camphor" and questioned its identity with benzoic acid. The first publications occupy themselves principally with the occurrence in, and the production from, different plants. Some authors gave $C_{10}H_6O_2$, others $C_9H_7O_2$, as formula based on the results of their analysis. The correct composition, $C_9H_6O_2$, was recognized in the middle of last century by Gerhard and Bleibtreu und likewise by Dumas. The indications of the m. p. differ considerably, 40, 50, 120° and other figures being given; the correct value of 67° was only found in 1862 by Zwenger and Dronke. At that time, there still existed a complete uncertainty as to the chemical constitution of coumarin, and even after Perkin had carried out its synthesis, in 1868, *i. e.* nearly half a century after Vogel's discovery, the explanation of the structure was at first incorrect. Perkin was able to state already at the time that coumarin is only a link in a series of homologous bodies that may be prepared from the sodium compound of salicylaldehyde and the homologous acid anhydrides. He obtained in this way such a series of homologous coumarins, which he designated according to the anhydride used, and investigated the propionic, butyric, and valeric coumarins. Perkin first took the coumarin synthesized by himself for a mixture of acid radicals, consisting in acetylo-"diptyl", $CH_3CO \cdot C_7H_3O$. The correct formula was established by Fittig about 1870 as that of an hydroxy-cinnamic anhydride, which view has been confirmed by later investigations. Perkin's coumarin homologues could then be explained as methyl, ethyl, &., coumarins. In the section "Characteristics of coumarin" it is put forth that several of the coumarin derivatives are of general or scientific interest and partly occur in nature, such as umbelliferone (7-hydroxy-coumarin), citropten or limettin (5,7-dihydroxy-coumarin monoethyl ether), bergaptene (hydroxy-coumarino-furane methyl ether), &c. The occurrence of coumarin in nature, the various synthesis and the physical and chemical properties are discussed in detail. Besides, the monography contains a comprehensive review of the coumarin derivatives, the number of which is so considerable that one might speak of a coumarine series the same as of a benzene series. Taking into consideration that coumarin consists

[1]) Prof. Dr. H. Simonis, *Die Cumarine*, Stuttgart 1916, 298 pages. Price ℳ 12.— in paste, ℳ 13.— bound in linen.

of an α-pyrone ring combined with a benzene nucleus, it becomes evident that it is the mother-substance of so long a range of compounds.

C. D. Harries, on retiring from his office as a university teacher, has published in the form of a book his meritorious works on ozone and its action on organic compounds[1]). Many of them deal with bodies closely connected with our special domain, but as they have nearly all been discussed in our *Reports* in the course of time, we may here limit ourselves to mention the new book.

D. Wagner, in a treatise *"Wundheilung mit ätherischen Ölen"* (Berlin and Vienna 1915), describes numerous cases of illness from his experience in the surgical department of a hospital, in which solutions of essential oils have had excellent effect. Guided by the results of numerous experiments, Wagner uses a mixture of oils of cinnamon, cloves, *Eucalyptus Globulus,* myrrh, turpentine together with menthol, thymol, camphor and balsam of Peru, dissolved in equal parts of linseed and cod liver oils. To this solution, he adds 0.25 per cent. of iodine and 1 per cent. of said oils and stearoptenes mixture, previously saponified with potassium hydroxide. Wagner has observed that the disinfecting power of essential oils is considerably increased by making their solution alkaline or at least neutral. The manufacture of the mixture as such, as potash soap and in "gelodurat" capsules has been reserved to a pharmacist, on the alleged reason that the test of essential oils as to their purity was so difficult and the saponification process so complicated. The preparations are sold under a fancy name. As regards the difficulty of verifying the purity of the oils, the author seems to ignore that absolutely pure qualities can be obtained in the trade easily and by everybody.

It would lead us too far to discuss the numerous cases reported as having favourably been influenced by the mixture of essential oils, the quantitative composition of which Wagner does not indicate.

Analytical Notes.

In order to ascertain small quantities of essential oils in extracts, cordials, &c., A. G. Woodman, R. T. Gookin and L. J. Heath[2]) have worked out a method depending upon the use of a nephelometer[3]). If water be added to an alcoholic solution of volatile oils, an emulsion is formed which appears white, as it consists of small globules of oil which are capable of reflecting the light. The amount of light reflected by the emulsion is compared with that of a standard of known concentration. The authors used a Duboscq nephelometer, but slightly modified it. Concerning its construction, we would refer to the original, as it is difficult to give an abstract of the description. Good results were obtained with oils of peppermint, nutmeg, aniseed and roses. In the investigation of cordials the sugar content is rather disturbing, as the oils do not separate quantitatively. The standard used for comparison must, in similar cases, contain about the same amount of sugar as the cordial. If the cordials are strongly coloured, the alcohol and essential oils must sometimes be distilled off and the

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[1]) C. D. Harries, *Untersuchungen über das Ozon und seine Einwirkung auf organische Verbindungen.* 720 pages with 18 illustrations in the text, Berlin 1916. — [2]) *Journ. Ind. Eng. Chemistry* 8 (1916), 128. — [3]) The determinations with the aid of the nephelometer consists in finding out the thickness of the layers of two suspensions of one and the same substance that reflect an equal amount of light.

quantity of the latter determined in the distillate, containing, of course, the same amount as the cordial.

Another method has been described by C. F. Muttelet[1]). He adds 75 cc. of water to 200 cc. of liqueur and distils off 200 cc. of the mixture. He puts these together with 50 grams of common salt and 10 cc. of light petroleum (b. p. about 40°) into a separating funnel holding about 300 cc. and shakes till 10 minutes after the salt has dissolved, adding a few cc. of water, if required. He then shakes the solution twice again with 5 cc. of light petroleum, cautiously evaporates the light petroleum collected and weighs the residue until the weight is constant. Losses are not to be feared, provided the evaporation is carried out with due care.

The use of benzyl alcoholic instead of ethyl alcoholic potash lye for the saponification of essential oils.

The quantitative estimation of esters in fatty and essential oils is, a well-known fact, carried out by boiling with N/2 potash lye and titrating the excess of alkali back with a N/2 acid. The saponification takes 1 hour on an average, it being necessary only in quite isolated cases to heat longer in order to split the esters completely[2]).

The process is shortened considerably, according to H. F. Slack[3]), if instead of ethyl alcohol benzyl alcohol is used for preparing the potash lye. In the case of lavender oil, the saponification was completed after only 5 minutes. This is due to the fact that the reaction takes place at a much higher temperature, ethyl alcohol boiling at 78°, benzyl alcohol at 205°. In consequence, the saponification is not carried out on a water-bath, but over an open flame. It is best to use N/2 or N solutions, a higher concentration not being applicable, it is said. As benzyl alcohol itself sometimes shows small acid and ester values, these must previously be determined and taken into consideration, all the more when the benzyl alcohol serves also as a diluent for the oil. After the saponification is complete, the mixture is allowed to cool down to about 100°[4]), diluted with a suitable volume of neutralized methyl alcohol and titrated back by means of N/2 acid.

In order to determine the free acid contained in the oil, Slack uses alcoholic N/10 potash lye, as in an aqueous preparation the water would defer the saponification in case the acidity was rather considerable. When using ethyl alcoholic lye he prefers a N to a N/2 solution, as the saponification is then completed in half an hour, whereas it would otherwise take an hour, this being proved with a lavender oil.

This observation does not tally with our own, for we have stated that in the case of linalyl acetate and bergamot oil[5]), when in the main the same ester is concerned as in oil of lavender, N/2 lye quantitatively saponifies the ester in half an hour.

W. H. Simmons[6]) reports on the formylation[7]) of volatile oils. He found from 45 to 57 per cent. of citronellol in Réunion geranium oil and from 32 to 43 per cent. in the African variety. The results of the formylation of several oils are given in the form of tables, some of the oils having been treated with formic acid of 85 instead of 100 per cent. His experiments have shown that terpineol is almost completely destroyed through formylation; geraniol and linalool are converted into esters to a

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[1]) *Annal. de Chim. analyt.* **21** (1916), 50. As to other ways of estimating essential oils in liqueurs, see *Reports* April **1915**, 49; October **1915**, 7. — [2]) See Gildemeister and Hoffmann, *The Volatile Oils*, 2nd. ed., vol. I, p. 572. — [3]) *Chemist and Druggist* **87** (1915), 673. — [4]) Methyl alcohol boiling at about 65°, it seems advisable to cool a little farther. — [5]) *Report* April **1910**, 60; October **1910**, 60. — [6]) *Analyst* **40** (1915), 491. — [7]) See *Report* October **1913**, 64.

very great extent, but santalol is only partly attacked. Citronellol, menthol and even borneol (the latter in oil of rosemary) may be determined approximately by formylation. If the directions given are closely followed, the menthol content of peppermint oil may likewise be determined by formylation. Simmons sees the advantage of the formylation method in that heating on a water-bath suffices, there being no need to add any catalyst.

A. Hahn[1]), in a small treatise, discusses the various methods used in the perfume chemistry in order to test for chlorine compounds. These are the Beilstein, the lime and the combustion tests. We should not go into this well-known matter any further, if it was not necessary to oppose one of Hahn's assertions which might mislead. He declares Beilstein's test as the most delicate of the three and considers a substance as absolutely free from chlorine, if following this method no chlorine can be ascertained. We have remarked on previous occasions[2]) that, whenever minimal quantities of chlorine are concerned, Beilstein's test is inferior to either the lime and the combustion tests in accuracy and reliability, which we cannot but confirm once more. A negative result of Beilstein's test has never been for us a sure proof for the absolute absence of chlorine in a preparation, and we have pretty often observed that our doubt was justified.

Hahn correctly mentions that Beilstein's test fails in the presence of substances containing benzoic acid, as the copper benzoate, formed on heating with copper oxide, is somewhat volatile and colours the flame green, thus foreshadowing a content of chlorine. In his view, however, that the same holds good for substances containing camphoric acid, he is in opposition to H. Kunz-Krause[3]), who lays stress upon the fact that camphoric acid does not yield any volatile compound with copper, therefore leaving the Bunsen flame unaffected.

In the cumbustion method, which Hahn erroneously calls Schimmel's method[4]), he departs from the usual way of execution in that he collects the combustion products in a funnel of about 1 litre capacity, instead of a beaker.

Determination of esters in citrus oils. In order to determine the contents of volatile esters in citrus oils, A. R. Albright and C. O. Young[5]) proceed as follows: From 100 grams of oil, contained in a Ladenburg flask, the limonene is slowly (18 to 20 drops per minute) distilled off at from 2 to 5 mm. pressure. The flask is then connected with a long condenser and steam passed through until 200 cc. of water have passed over. This ought to take at least 30 to 45 minutes, the liquid in the flask being meanwhile kept at a constant volume by heating with a small flame. If one distils more quickly, some less volatile constituents nearly always pass over, causing turbidity and making titration more difficult. The same is the case if the quantity of liquid in the flask becomes too small. If, on the other hand, too much water collects in the flask, the result will be too low, on account of the incomplete evaporation of the esters. The distillate always reacts slightly acid towards phenolphthalein, but no relations between acid content and saponification value could be found.

In the presence of sodium acetate, semicarbazide hydrochloride, in the theoretical quantity or in excess, is added to the distillate. The quantity of semicarbazide hydrochloride may be deduced from the citral content, determined for the purpose according

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[1]) *Deutsche Parf.-Ztg.* **2** (1916), 95. — [2]) *Reports* October **1908**, 13; April **1912**, 151. — [3]) *Apotheker Ztg.* **30** (1915), 142; *Report* October **1915**, 56. — [4]) We have pointed out already in our *Report* of October **1890** (page 5, foot-note) that the method does not originate from us; as far as we know, it was first published in one of Gehe & Co.'s trade reports. — [5]) *Journ. Americ. chem. Soc.* **37** (1915), 2382.

to Hiltner's method[1]). After 100 cc. of alcohol of 95 per cent. have been added, the mixture is shaken for a few minutes and then left to stand for 10 to 15 minutes, or even longer. Generally, a considerable quantity of citral semicarbazone will separate. As soon as the liquid is neutralized, 50 cc. of N/2 potash lye are added; one then boils it for two hours under a reflux condenser, cools quickly and titrates the excess of alkali with with N/2 hydrochloric acid. There is far more phenolphthalein necessary than in ordinary titrations. If 100 grams of oil be used, the number of cc. of N/2 potash lye consumed multiplied by 0.098 and the factor 1.28 will indicate the percentage of saponifiable substances, calculated as linalyl acetate.

As aldehydes are disturbing in this estimation, they are removed with the aid of semicarbazide hydrochloride. It resulted to be useless to filter off the citral semicarbazone, as one does not succeed in making the deposit of semicarbazone absolutely free from esters. The presence of the citral semicarbazone does not disturb the saponification; it does not use up any alkali, as has been proved by experiments. In order to obtain correct figures, the percentage of linalyl acetate must be multiplied by 1.28.

The method was tried as to its reliability on mixtures of known composition. In genuine lemon oils, ester contents from 1.24 to 1.74 per cent. were found in this way.

In our opinion this proceeding is not called upon to acquire many friends. Quite apart from the fact that it abounds with possibilities for errors, nobody can seriously be expected to waste 100 grams of either lemon or orange oil on each single estimation of esters which, by the way, is of secondary importance and may be carried out in the usual manner and with only 1.5 gram of oil exactly enough to show whether the oil tested has a normal ester v. or not. The content of aldehydes is so small in either case that it does not influence the ester v. to an extent worth mentioning. The presence of waxy matter does not interfere either, oil of bergamot being the best proof for this assertion, as the estimation of its ester v. has for long enough been carried out with the best success in the ordinary way.

The presence of some aldehydes proved by means of sulphanilic and naphthionic acids.

When studying the colour reactions of vanillin, E. P. Häussler[2]) observed that an intensely yellowish red colour appeared on mixing solutions of vanillin and sulphanilic acid. He went further into the matter and found that he had to deal with a condensation product of both components, presumably a benzylidene compound. P. Pooth[3]), who, owing to an agreement with Häussler, took up the study of analogous condensation products of aldehydes and sulphonated aromatic amido compounds, succeeded in confirming Häussler's supposition by proving that the condensation product of vanillin really is a benzylidene compound. Although the colour reactions of sulphanilic acid and aromatic aldehydes are very well noticeable, the use of naphthionic acid offers great advantages for qualitative purposes, as then said reactions are still more distinct. In most cases the reaction product crystallizes on cooling and may then be separated off for a closer investigation.

Pooth carries out the reaction as follows: 3 to 4 cc. of a 10 per cent. neutralized aqueous solution of the sodium salt of the sulphonic acid are heated in a porcelain dish on a water-bath. The aldehyde or the mixture, dissolved in 96 per cent. alcohol, are then added quite hot, when the colouring will take place immediately. It generally becomes more intense on evaporation. The same is the case very often, if a few

[1]) See *Report* October **1910**, 163. — [2]) *Zeitschr. f. anal. Chem.* **53** (1914), 363, 691; *Report* April **1915**, 61. — [3]) *Schweiz. Apotheker Ztg.* **54** (1916), 377.

drops of dilute sulphuric acid are added to the cold reaction mixture, diluted with water, but sometimes the colour changes altogether.

The following colorations were noticed, when using sulphanilic and naphthionic acids: —

	sulphanilic acid	naphthionic acid
benzaldehyde	almost colourless	yellow
o-hydroxybenzaldehyde (salicylaldehyde)	yellow to pale orange	yellow with a shade of green
anisaldehyde	pale pink; yellowish red on evaporation	dirty yellow
vanillin	orange-yellow	brownish yellow; on addition of sulphuric acid: beautifully yellow
piperonal (heliotropin) .	almost colourless; evaporated or with sulphuric acid: yellow	on evaporation greenish yellow
cinnamaldehyde . . .	vinous yellow; with sulphuric acid: orange to scarlet	strongly yellow; with sulphuric acid: orange red
cuminaldehyde . . .	dirty vinous yellow	pale vinous yellow

Colorimetric estimation of cinnamaldehyde in cinnamon and of vanillin in vanilla.

According to Tschirch[1]), the value of cinnamon bark is inversely proportional to the number of the mucous cells and in direct proportion to the number of oil cells. But as Th. von Fellenberg[2]) has found, cinnamon must not be considered as inferior from the very outset, only because it is rich in mucus. Besides, not only the oil content in itself, but in the first line the content of cinnamaldehyde, the characteristic constituent of the oil, is of importance for the valuation of cinnamon bark. In order to estimate the cinnamaldehyde in cinnamon, von Fellenberg indicates a colorimetric method, based on the reaction of cinnamaldehyde with concentrated sulphuric acid and *iso*butyl alcohol, when the latter is transformed into *iso*butylene. The solutions required are: 1. Alcohol of 38 per cent., obtained by adding water to 40 cc. of 95 per cent. alcohol up to 100 cc. 2. A 5 per cent. solution of *iso*butyl alcohol in 95 per cent. alcohol. The *iso*butyl alcohol must be pure, no coloration to be shown on adding to the solution twice its quantity of concentrated sulphuric acid. 3. A checking solution of 0.02 per cent. cinnamaldehyde[3]) in alcohol of 38 per cent. It is made by dissolving $\frac{20}{n}$ grams of the bisulphite compound of cinnamaldehyde per litre, when n means the content of cinnamaldehyde in the compound. The bisulphite compound has been chosen, as it is very stable, in opposition to pure cinnamaldehyde; there was no alteration after 25 days, and the standard solution was likewise intact. The content of cinnamaldehyde in the compound is estimated by titration with bromo-iodine. For this purpose, 0.1 gram of the bisulphite compound, finely powdered, is mixed with 100 cc. of a N/50 solution of bromate-bromide and 10 cc. of concentrated hydrochloric acid. After 20 minutes, 3 cc. of a 10 per cent. potassium iodide solution are added and the mixture is titrated back with N/50 sodium thiosulphate solution; 1 molecule of the bisulphite compound

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[1]) *Handbuch der Pharmakognosie*, vol. II, page 1268. — [2]) *Mitt. Lebensmittelunters. u. Hyg.* **6** (1915), 254. — [3]) von Fellenberg writes on page 265 "standard solution of 2 per cent. cinnamaldehyde in alcohol of 38 per cent.", which is not correct, as may be deduced from the whole treatise and particularly from the description of how the solution is made.

requires 4 atoms of bromine. Besides, a mixture of 1 gram of the bisulphite compound, 50 cc. of N/50 iodine solution and 2 cc. of hydrochloric acid is heated up to 50° C. for 6 to 7 minutes. After cooling, the titration is carried out in the usual way; 1 molecule of the compound requires only 2 atoms of iodine, as this only oxidizes the sulphurous acid but does not act on the double bond of the cinnamaldehyde molecule. The content of cinnamaldehyde is then calculated from the difference between the consumption of bromine and iodine, as 1000 cc. (*N*-bromine solution — *N*-iodine solution) correspond to half a molecule $= \frac{132.1}{2}$ gram of cinnamaldehyde. The pure cinnamaldehyde bisulphite compound must use up exactly twice as much bromine as iodine. If more iodine be consumed, a corresponding quantity of benzaldehyde bisulphite compound and sodium sulphite is present. The presence of a little benzaldehyde does not influence the shade of colour and may, therefore, be neglected.

In order to estimate the cinnamaldehyde in cinnamon, one proceeds as follows: 1 gram of finely powdered cinnamon and 40 cc. of 95 per cent. alcohol are placed into a flask of 400 cc. capacity, which is connected with a condenser and a measuring flask of 100 cc. The mixture is kept slightly boiling for 10 minutes, after which time the alcohol is distilled off until only 5 to 10 cc. remain, when 100 cc. of water, previously boiled and therefore free from oxygen, are added. The distillation is then carried on fairly quickly, until the distillate, together with the alcohol that passed over in the beginning, comes up to nearly 100 cc. One then adds the difference, so as to obtain fully 100 cc., and pours 5 cc. of the distillate, together with 2 cc. of the solution of *iso*butyl alcohol and 3 cc. of alcohol of 38 per cent., into a measuring flask of 100 cc. Holding said flask a little inclined, one carefully adds 20 cc. of concentrated sulphuric acid, shakes the mixture and then allows it to rest for $^3/_4$ of an hour. 5 cc. of the type solution are treated in the same way. The colorations are then compared in the colorimeter (Duboscq's being the best). It is permissible to dilute with dilute sulphuric acid (2 vols. of concentrated sulphuric acid and 1 vol. of water) to the extent required. The intensity of coloration found is multiplied by 2, and the corresponding percentage of cinnamaldehyde may then be read from tables that accompany the publication.

The percentages of cinnamaldehyde in the materials tested were: 1.31 to 1.84 per cent. in Ceylon cinnamon, 1.01 to 1.05 per cent. in cinnamon chips, 1.23 to 2.77 per cent. in cassia bark and 3.77 per cent. in *flores cassiæ*.

The same author[1]) likewise describes a colorimetric method of estimating vanillin in vanilla, founded, as in the case of cinnamaldehyde, on the coloration resulting when vanillin is brought together with concentrated sulphuric acid and *iso*butyl alcohol. When sampling, due regard must be given to the fact that the vanillin is not quite evenly distributed in the vanilla bean. According to von Fellenberg, a good average is obtained by taking either the middle piece or two pieces equally far apart from the centre piece.

The following description of the method is given: The vanilla bean is weighed and an average sample selected as indicated (about 1 gram). Its weight must be determined quite exactly. This sample is cut in transversal sections of 1 to 2 mm. thickness, but which ought still to hang together in one spot, quantitatively placed into a small flask and extracted 4 times under a reflux condenser with altogether 90 cc. of water, by boiling each time for 3 to 5 minutes and pouring the slightly cooled extract into a measuring flask of 100 cc. From and after the second extraction, one expresses

[1]) *Mitt. Lebensmittelunters. u. Hyg.* **6** (1915), 267.

the vanilla pieces on the funnel and finally kneads them several times with a few cc. of water. The brown extract is brought up to 100 cc., vigorously shaken with 0.5 gram of Fuller's earth and then filtered. 50 cc. of the filtrate are shaken 5 times with ether free from alcohol, 50 cc. of ether being used the first time and 25 cc. for each treatment afterwards. The ethereal solution is dried over calcium chloride for from 5 to 10 minutes, filtered under rinsing with ether, the latter then being removed by distillation and, at last, by blowing air through. One heats the residue with 30 cc. of water to 50 or 60°, in order to separate the vanillin from the small particles of wax dissolved, pours it into a measuring flask of 100 cc., rinses, fills up to the mark and filters. To 5 cc. of the filtrate, in a measuring flask, 5 cc. of a 1 per cent. solution of *iso*butyl alcohol in 95 per cent. ethyl alcohol are added and afterwards 20 cc. of concentrated sulphuric acid are allowed to flow in, the flask being held slightly inclined. One then shakes and allows the mixture to stand for 45 minutes. In a similar way a type solution is treated, which has been obtained by dissolving 0.1 gram of pure, recristallized vanillin, previously dried until the weight remained constant. The colorations resulting are compared in a colorimeter, it being admissible to dilute the solutions with dilute sulphuric acid (1 vol. of concentrated sulphuric acid and 1 vol. of water). The vanilla content amounts to $\frac{4a}{g}$, a corresponding to the number of mgs. of vanillin found in the final solution and g to the weight, in grams, of the vanilla used. The value a is obtained with the aid of tables accompanying the treatise.

The vanillin content thus determined for Bourbon vanilla oscillated between 2.35 and 3.03 per cent., an inferior kind only containing 1.54 per cent.

In case the vanilla is suspected to have been fraudulently covered with vanillin, it is advisable to test the outer and inner layers separately, when normal vanilla will not show any great differences.

It remains to be seen in how far the methods described will be adopted in analytical practice. As far as we are concerned, we hold that a colour reaction will always be, especially for quantitative estimations, a mere makeshift, which one is glad to dispense with if there are more exact tests available. This is the case for either cinnamaldehyde and vanillin, for the quantitative estimation of which J. Hanuš published some time ago very useful and reliable methods, according to which cinnamaldehyde[1]) is brought into reaction with semioxamazide and vanillin[2]) with β-naphthylhydrazine or, better still, with *p*-bromophenylhydrazine. These methods are specially suitable for the quantitative determination of small quantities of the aldehydes in question, such as are present in the respective drugs, and have at least the advantage over Fellenberg's tests that they are exactly quantitative estimations in the literal meaning of the word, the results of which do not depend upon the subjective impression of the individual observer.

We consider recommendable, however, the way of sampling the vanilla and that of extracting, previous to the distillation of the cinnamon, the cinnamaldehyde with alcohol, the quantity of which may be reduced to one quarter for the semioxamazide determination. As to the distillation itself, we prefer it with a strong current of steam.

Hanuš[3]), at the time, determined the following percentages of cinnamaldehyde in various cinnamon barks: Ceylon cinnamon 1.74 to 2.19 per cent., chips 1.23 to 1.42 per cent., cassia bark 2.08 to 3.81 per cent., *flores cassiæ* 3.70 to 6 per cent., bark

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[1]) *Zeitschr. Untersuch. d. Nahrungs- u. Genussm.* **6** (1903), 817. — [2]) *Ibidem* **3** (1900), 531. — [3]) *Ibidem* **7** (1904), 671.

of *Cinnamomum Tamala* (East Indian cinnamon) 1.80 per cent, bark from branches of wild Ceylon cinnamon 0.12 per cent., bark from the trunk of wild Ceylon cinnamon 1.31 per cent., clove cinnamon *(Cassia caryophyllata)* 1.51 per cent.

Regarding the components of vanilla, we would amend von Fellenberg's indications (*loc. cit.*, page 269) as to the presence of piperonal (heliotropin). Basing his assertion on Tschirch's "*Handbuch der Pharmakognosie*" (2nd. vol., page 1304), von Fellenberg says that, in addition to vanillin, vanilla likewise contains piperonal, the latter being even the chief aromatic of vanillons. What we have to say is, that, so far, nobody has proved the presence of piperonal in vanilla beans, and even as far as vanillons and Tahiti vanilla are concerned there is only W. Busse's[1]) supposition that, in addition to vanillin, they might contain piperonal. H. Walbaum[2]) proved later on that the aromatics of Tahiti vanilla, apart from vanillin, chiefly consisted in anisic alcohol, there being, besides, small quantities of anisaldehyde and anisic acid. However, no trace of piperonal was discovered. In Tschirch's book, the presence of piperonal is likewise merely mentioned as a supposition, and even with regard to Tahiti vanilla it is said that Busse "presumes" in it 0.16 to 0.073 per cent. of piperonal.

L. van Itallie, M. Kerbosch and A. P. Olivier[3]) report on the estimation of water in drugs. Generally, the water content is found by ascertaining the loss of a substance in weight by drying in a drying cupboard. However, if there are also other volatile components, there is a great danger that they may likewise evaporate. This is the case with the drugs containing essential oils, when it becomes necessary to determine the water as such, in order to arrive at correct figures. This is possible with a distillation method, according to which the substance under examination is distilled with liquid paraffin, toluene, xylene or light petroleum and the separating water, measured. The authors have not obtained satisfactory results with the carbide method, according to which the quantity of acetylene is measured, which is evolved on bringing the drug together with calcium carbide.

For some drugs, the contents of water and of essential oil were determined before and after drying. The determination of the content of essential oil was carried out as recommended by Beckmann and Danckwortt[4]), when the depression of an extract of the drug, made by means of ethylene bromide is compared with the depression of a similar extract, made after the drug had been deprived of its essential oil by steam distillation. The difference corresponds to the depression due to the essential oil, the percentage of which can then easily be calculated. The content of water was established after drying the drug: 1. at 50°, 2. at 50° and then at 103 to 105°, 3. at once at 103 to 105°, 4. in the sulphuric acid desiccator, 5. in the evacuated sulphuric acid desiccator and finally, by distillation with liquid paraffin, toluene, xylene and light petroleum. If liquid paraffin be used, its high b. p. disturbs in that water is split off from the drug at that temperature, so that the value found is too high. The differences found for cinnamon according to the cryoscopic method were too small to permit of ascertaining the content of essential oil. When black pepper is distilled, piperidin and ammonia are evolved, as is well known.

The distillation method gives the best results if xylene and toluene are used; with light petroleum, the figures are too low; with paraffin, as stated before, too high.

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[1]) *Arbeiten a. d. Kaiserl. Ges. Amt.* **15** (1898/99), 107. — [2]) *Wallach-Festschrift*, page 649, Gottingue, 1909; *Report* October **1909**, 142. — [3]) *Pharm. Weekblad* **52** (1915), 205. — [4]) *Arch. der Pharm.* **245** (1907), 211; *Reports* October **1906**, 104; October **1907**, 114.

The values found are compiled in the following summary: —

Contents of water and essential oil in some drugs.

	cloves per cent.	aniseed per cent.	mace per cent.	cinnamon per cent.	black pepper per cent.
content of water	8.0	10.5	7.5	11.7	12
content of essential oil	22.2	1.9	11.0	—	—
total loss on drying at 50°	11.6	6.8	12.3	9.7	—
loss of essential oil	6.99	—	6.7	—	9.8
total loss on drying at 50° followed up by drying at 103 to 105°	26.0	11.2	17.9	—	—
loss of essential oil	20.9	1.4	5.9	—	—
total loss on drying at 103 to 105°	29.5	11.2	18.6	12.7	12.7
loss of essential oil	20.9	1.4	7.9	—	—
total loss in the desiccator	7.9	6.7	10.9	10.4	10.37
loss of essential oil	2.6	—	4.6	—	—
total loss in the evacuated desiccator	8.6	10.6	14.4	11.0	—
loss of essential oil	2.1	—	5.8	—	—
total loss in the lime desiccator	—	5.9	8.9	—	—
loss of essential oil	—	—	3.4	—	—

Physical Notes.

The usual distilling apparatus of commerce are generally not adaptable to the distillation of essential oils *in vacuo*, especially if some considerable quantity of oil is to be fractionated. In such cases, a receiver described by M. T. Bogert[1]) and which, although somewhat different in form, has been used in our laboratories for a good many years already, will prove very useful. With the aid of this apparatus, any quantity of volatile oil may be fractionated without interrupting the process[2]). The apparatus consists of a cylindrical receiving chamber, A, graduated in cc. and with a funnel stem through which the distillate collected in A may be removed at will by opening the plain cock F. On one side of this receiving chamber, near the top, is the opening B, for the end of the condenser. From the top of the receiving chamber A, the tube C passes to the pump P and to the outer jacket E of the funnel stem. On this tube C, there is a plain cock at H, and a 3-way cock with offset ports at D. By turning this 3-way cock 90°, connection is established, by means of a perforation in the stem of the cock, between the air and, through the outer jacket E, the lower receiving vessel. In this way the atmospheric pressure can be restored to the lower vessel without in any way affecting the vacuum throughout the rest of the distilling system. When the first fraction has been collected in A, and its volume read, it can be run into the lower receiving vessel simply by opening the stopcock F. Then the stopcocks F and H are closed, and the 3-way cock turned so as to close the connection between the lower receiver and the pump and open that to the outer air.

Bogert further describes an apparatus of a somewhat simpler form, for use in laboratories which happen to be equipped with more than one pump.

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[1]) *Journ. Ind. Eng. Chemistry* 7 (1915), 785. The author kindly sent us a reprint. — [2]) A picture of the apparatus and a detailed description are given in the original and in the *Chem. Zentralbl.* **1915**, II. 1273.

Kubierschky[1]) in a treatise "On the relations of temperature and pressure of saturated vapours", gives a new formula for the relation between pressure and temperature of saturated steam. After mentioning the equations formulated by Clapeyron, Zeuner, Clausius and Callendar, in which in addition to pressure and temperature other properties of steam are taken into consideration, the author discusses Biot's, Schlemüller's and Bertrand's interpolative equations and afterwards van't Hoff's and van der Waals' equations of condition. The equation constructed by Kubierschky according to the steam pressures compiled in Landolt-Börnstein's book, 4th edition, runs as follows: —

$$\lg p_t = \frac{5.1148\ (t - 100)}{t + 230.39}.$$

It is, indeed, very simple, but shares with many others the disadvantage of depending somewhat upon temperature. Thus the value 230.39 is to be calculated at

232 for 0: 50: 300°
229 „ 0: 200: 300°
233 „ 0: 100: 374°

Not quite so exact, but sufficient for practical purposes, are the following abbreviated equations: —

$$\lg p \text{ (in atmospheres)} \ldots = \frac{5.1\ (t - 100)}{t + 230},$$

$$\lg p \text{ (in 1/1000 atmospheres)} = \frac{5.1\ (t - 100)}{t + 230} + 3,$$

$$\lg p \text{ (in kilos/sq. cm.)} \ldots = \frac{5.1\ (t - 99.1)}{t + 230},$$

$$\lg p \text{ (in mm. Hg)} \ldots = \frac{5.1\ (t - 100)}{t + 230} + 2.881 \text{ or}$$

$$\lg p \text{ (in mm. Hg)} \ldots = \frac{8\ (t + 19)}{t + 230}.$$

The pressures of saturated steam, calculated according to these abbreviated formulas, deviate by 1 to 1.18 per cent. within the temperatures of from 15 to 30° C. Otherwise, the deviations from — 16 to 300° C. are less then 1 per cent., on an average only about ½ per cent.

The result awakens a certain theoretical interest, as in spite of numerous attempts there was not, so far, such a simple interpolative formula for the calculation of the pressure of saturated steam at a temperature given. In its dependence upon temperature, it resembles the other known p,T-equations, which fact strengthens the supposition that liquid water too, as the various kinds of ice, possesses a different molecular constitution according to temperature.

The author believes that his abbreviated formula is suitable for engineering, but, in our opinion, it would be more advantageous to use tables instead of calculating the desired pressure in each case.

W. P. Jorissen and J. A. Vollgraff's treatise[2]) on the electric conductivity during the oxidation process of benzaldehyde and pinene, discussed on page 63 of our previous *Report*, has now been published elsewhere[3]). So far, except in flames, a distinct dispersion of the electric charge during the oxidation process had only been noticed in the case of phosphorus (phosphorus trioxide), whereas all attempts to prove that the

[1]) *Zeitschr. f. angew. Chem.* **29** (1916), I. 305. — [2]) *Chem. Weekblad* **12** (1915), 93. — [3]) *Zeitschr. f. physik. Chem.* **90** (1915), 553.

air had been ionized owing to the oxidation of other substances had failed. It results, however, quite clearly from Jorissen and Vollgraff's latest investigations, as mentioned by us at the time, that the oxygen becomes a conductor of electricity owing to the oxidation of pinene and benzaldehyde.

The addition-product camphor-chloralhydrate.

There is a pharmaceutical preparation, known under the name of camphor-chloral *Chloralum camphoratum*, which is composed of equal parts by weight of camphor and chloral hydrate and presents itself in the form of a highly viscous liquid. In order to ascertain whether the components form a solution or an additive product, E. Tsakalotos [1]) thermically analyzed the mixture, determining the sol. p^s. of varying mixtures of camphor and chloral hydrate. In the curve of sol. p^s., he obtained neither a eutecticum nor a maximum, as the mixtures containing between 30.5 and 57.59 per cent. of camphor were viscous to such an extent as to solidify glass-like, without crystallizing, it therefore being impossible to fix exactly the sol. p^s. As the components, camphor and chloral hydrate, if pure, do not solidify in a similar way, the author concludes that the mixture in question may be considered to be an additive product. Tsakalotos and Ph. A. Guye [2]) further explained this view when dealing with an investigation of acetone-chloroform.

Thermo-analytical examination of camphor-phenol, camphor-β-naphthol, and camphor-resorcinol.

In the treatment of surgical infections, a mixture of camphor and anhydrous carbolic acid is known, which contains up to 50 per cent. of phenol. The mixture is called Chlumsky's solution. It is antiseptic, but does not corrode the skin like carbolic acid. R. Kremann, F. Wische and R. Paul [3]) thermo-analytically investigated this camphor-phenol, as well as camphor-β-naphthol and camphor-resorcinol, *i. e.* camphor with three different phenols.

Molecular additive products of phenols and ketones are frequently known. With some couples of bodies there is no reaction, at least it is no so general as between phenols and amines. The authors used *d*-camphor for their investigations. They found that the curve of the sol. p^s. of varying mixtures of camphor and resorcinol shows a maximum between two eutectic points, indicating that the two bodies combine. They were, however, unable to establish completely the curves of the sol. p^s. of camphor-phenol and camphor-β-naphthol, as the concentrated solutions solidified glass-like and the exact sol. p. could not be observed. Nevertheless, the authors suppose that the components combine in each case. They mention that Caille [4]) proved already the camphor-resorcinol to be an equimolecular compound. On the other hand, it escaped their attention that J. Kerfoot Wood and J. Drummond Scott [5]) proved beyond doubt, by a complete curve of sol. p^s., that an equimolecular additive product was likewise formed by camphor and phenol, and that there is only this one compound, not two, as Léger [6]) pretended to have found.

The fact that Chlumsky's solution does not corrode is, however, not explained by the proof that there is a compound, for in the first instance it is so labile that even in a 50 molecular per cent. composition the solution always contains compound as

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[1]) *Journ. de Pharm. et Chim.* VII. **12** (1915), 355. — [2]) *Journ. de Chim. physique* **8** (1910), 340. — [3]) *Monatsh. f. Chem.* **36** (1915), 911. — [4]) *Compt. rend.* **148** (1909), 1458. — [5]) *Journ. chem. Soc.* **97** (1910), II. 1573. — [6]) *Compt. rend.* **111** (1890), 109.

well as free camphor and free phenol, and, besides, the corrosive action of the latter is likewise decreased by addition of thymol, although such a mixture, as has been proved, does not contain any compound. The authors explain, most likely with reason, the mild action of camphor-phenol, in comparison with liquid carbolic acid, by the absence of water.

They mention, besides, that Chlumsky himself sees the cause in the quick evaporation of the camphor. Kremann and his collaborators likewise seem to suppose that camphor escapes more quickly from the liquid mixture than phenol. The well-known fact that camphor evaporates remarkably quickly, in spite of its high b. p. of 206.0° at a pressure of 760 mm., has a special reason, which may here be discussed for once. If two volatile bodies be allowed to evaporate, the extent of the volatilization during a given time depends upon their b. p^s. and their surfaces exposed, as the evaporation only takes place on the surface. If camphor be melted like the anhydrous phenol and made to solidify as a whole, one would find that phenol volatilized far more quickly, owing to its low b. p. of 181.4° C.; *viz.*, nearly twice as quickly according to the two curves of vapour pressure. Generally, camphor presents itself as a rather finely granular crystalline mass, the surface of which is many times as large as that of the melted and then congealed phenol, so that it will naturally volatilize more quickly. The conditions are quite different, however, for a mixture of camphor with phenol, which at room temperature forms a homogenous, viscous liquid, when there is no difference in the surfaces of the two components. The free bodies, being present in the solution in addition to the higher boiling compound, volatilize according to their partial pressures at the temperature of the surrounding air, for this is a case of isothermic evaporation. The mixture, therefore, does not become richer in phenol in the course of time, as Chlumsky presumes, but richer in camphor. The compound is not left unaffected either by the evaporation, for the solution of uncombined camphor, uncombined phenol and compound is in a state of chemical equilibrium, which always rebuilds itself by decomposition of parts of the compound, whenever the free components escape.

Botanical Notes.

In an article by E. Gilg[1]), entitled *Über die Duftstoffe liefernden Pflanzen* ("On plants yielding perfumes") there are to be found notes of general interest concerning the production of aromatics, especially in the South of France, the formation and location of volatile oils in the plant, and the cultivation and the forms of vegetation of the aromatic plants. Besides, there are statistics.

Fungus disease of the grape-fruit tree.

On pages 65 and 66 of our previous *Report,* we discussed some fungus diseases of lemon and orange trees, in addition to which we would now mention another such disease, which has been observed on the Isle of Pines, south of Cuba. There is a large plantation there of citrus trees, mostly grape-fruit trees (*Citrus decumana,* L.)[2]), covering 1200 acres. It was created in 1909, and already in 1914 it became necessary to consult a specialist in order to avoid the tremendous losses caused by the rotting

[1]) *Deutsche Parf.-Ztg.* **2** (1916), 116, 145, 173. — [2]) Citrus Pathological Laboratory, San Pedro, Isle of Pines, published by the San Pedro Growers Company, Columbus, Ohio, U. S. A. First annual Report; *Perfum. Record* **6** (1915), 348.

of the fruit during the transport. The cause has been found in a *Diplodia* species, a fungus which attacks the trunks, the branches and the leaves and causes the ripe fruits to rot. The only remedy known so far is to keep the trees otherwise in perfect condition, so as to increase their power of resistence.

Lignum nephriticum. Some time ago, H. J. Möller[1]) pronounced the opinion that the so-called *Lignum nephriticum* originated from the leguminous plant *Pterocarpus Amphymenium,* DC., whereas according to J. Small[2]) *Eysenhardtia amorphoides,* H. B. et K. *(Leguminosæ)* is said to be the mother-plant of the drug. As W. E. Safford[3]) recently stated in the Botanical Society of Washington, the mother-plant is *Eysenhardtia polystachia*[4]), which occurs in Mexico but is not taken much notice of.

A botanical investigation of the kinds of vanilla cultivated in Tahiti has been discussed on page 80 of this *Report.*

Phyto-physiological Notes.

In an article, entitled "earthy smell", H. Kühl[5]) discusses the works of Berthelot and André, Rullmann and Salzmann[6]) on the odour emanating from earth, when dug over. Berthelot and André tried to explain it by the occurrence, in the soil, of an organic compound volatile with steam. Rullmann succeeded in tracing it back to biological causes and isolated from various soils, as producer of the smell, a bacterium which he called *Cladothrix odorifer.* This was recognized later on as a radiated fungus and called *Actinomyces odorifer.* Interesting is the fact that on nutrient gelatin odourless as well as odoriferous colonies are formed. If such odourless colonies were transferred on a nutritive medium rich in carbohydrates, such as sterilized pulp of soaked bread or peas, the odour was formed again. It is certain, therefore, that carbohydrates were decomposed by *Actinomyces* with formation of the aromatic to which the smell of the soil is due. In order to obtain this aromatic, Rullmann extensively reared the microbe in a one per cent. milk sugar solution. After three weeks, the earthy smell was strongly developed. The bacteria colonies were then distilled *in vacuo* at 25 to 30° C. and the fractions passing over first, collected separately; they had a very strong earthy smell and an acid reaction. By shaking them with ether, minute crystals were obtained, which refract the light rays twice and represent, in a chemically pure state, the aromatic contained in freshly dug-over spring and autumn soils.

Salzmann's publications tell us how, and under what conditions, the aromatic is formed in the field soil. Acids, which in addition to the carboxyl group contain either H, CH_3, CH_2 or CHOH, are disdained by *Actinomyces odorifer* as sources of carbon. Salzmann observed that the fungus grew considerably if the acids contained a second carboxyl group. In case the acids then contained at the same time the group CHOH, a further increase of the growth, combined with a powerful evolution of smell, was the consequence.

E. Herrmann[7]) published an article on the smell of mushrooms, containing useful hints regarding the gathering of mushrooms. Very often poisonous mushrooms may be distinguished from edible ones by their odour: however, it must not be forgotten

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[1]) *Berichte d. deutsch. pharm. Ges.* **23** (1913), 88; *Report* October **1913**, 69. — [2]) *Pharmaceutical Journ.* **92** (1914), 4; *Report* April **1914**, 68. — [3]) *Journ. Washington Academy of Sciences* **1915**, 503; *Chem. Ztg.* **39** (1915), 754. — [4]) This species is not mentioned in the *Index Kewensis.* — [5]) *Naturw. Umschau der Chem. Ztg.* **4** (1915), 102. — [6]) See *Chem. Zentralbl.* **1902**, I. 1069. — [7]) *Pharm. Zentralh.* **56** (1915), 555.

that the sensation of smell is an individual matter, so that an exact knowledge of the different kinds of mushrooms will be required when gathering them as food.

Generally speaking, there is little known as to the bodies which cause the smell of mushrooms. In some cases volatile oils have been isolated, *e. g.* from *Trametes suaveolens* and from *Boletus edulis;* besides, there is a camphor-like substance contained in the toad-stool, the amanitol described by Zellner[1]).

In some mushrooms the smell of aniseed is specially marked. It is very strong in *Clitocybe odora,* a greyish green mushroom growing on decaying leaves in thickets and the odour of which is noticeable within a radius of 10 metres; it is a good edible mushroom. The same smell is less pronounced in *Psalliota arvensis,* but of greatest importance, as it is sometimes the only means of distinguishing it from the highly poisonous *Amanita verna, mappa*[2]). *Lentinus cochleatus* likewise exhales a fairly strong aniseed smell; it is an innocuous mushroom, but cannot be eaten on account of its toughness. Another mushroom smelling of aniseed is *Polyporus suaveolens,* which grows on willows.

The smell of blue melilot *(Melilotus cæruleus, Trigonella cæruleum)* is conspicuous in *Lactaria helva.* This mushroom generally begins to smell after drying, but then very strongly and for a long time. The author pounded such mushrooms and left them for a year in an open dish, after which time their odour was still very strong.

Pholiota radicosa, Phœodon suaveolens and *Trametes odorata,* which latter grows on the stumps of conifers, smell of fennel.

Only one mushroom, *Marasmius caryophylleus,* reminds one of cloves. It is suitable for soups and as a condiment.

A cinnamon smell is found in *Clitocybe infundibuliformis, C. clavipes* and *Hydnum cyathiforme,* but it is little pronounced.

The smell of bitter almonds is found exclusively in *Russula fœtens,* but to some people it appears simply as nauseous.

A smell as of flour is common in a good many mushrooms and indicates almost invariably that they are edible, such as *Rhodosporus Prunulus, Limaceum eburneum, Entoloma prunuloides, Tricholoma graveolens, T. gambosum, T. equestre, T. flavobrunneum* and *T. portentosum.* A less frequent kind is *T. sejunctum,* which is bitter, however, and not edible therefore. *Clitocybe nebularis* likewise has a pronounced smell of flour.

A fruity smell is restricted to some edible pore fungi, such as *Boletus bovinus, B. subtomentosus* and *B. granulatus.*

An odour like balsam of Peru is characteristic for *Lactaria glycyosma.*

A smell of musk only occurs in truffles, fairly week in the summer species *(Tuber æstivum)* but very strong in the so-called Perigord truffle.

Lactaria camphorata reminds one of camphor, but only when dried.

A smell of onion or garlic is found in the so-called *"mousseron",* but it disappears completely after drying.

Many mushrooms, fresh or dried, have a spicy odour, which cannot easily be described in a more definite way. Dried mushrooms are, therefore, very suitable as condiments for sauces, soups, stews, &c.

Paxillus subtomentosus and *Polyporus giganteus,* both growing on tree stumps, have an acid smell.

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[1]) Gildemeister and Hoffmann, *The Volatile Oils,* 2nd. ed., vol. II, p. 1 and 2. — [2]) See E. Herrmann, *(Die Doppelgänger unter den Pilzen) Resemblances in mushrooms, Pharm. Zentralh.* **49** (1908), 557.

The stink-horn fungus is characterized by a pronounced carrion smell. Although it may contaminate the air for a considerable distance, it is said to be eaten when young.

A smell of raddish is frequent, but restricted almost entirely to fungi unfit for being eaten. It is specially noticeable in *Hebeloma crustiliniforme* and *Lepiota cristata*.

The smell of *Tricholoma sulfureum* may be called hemp-like.

A smell as of potato chits is an important characteristic of the highly poisonous deadly agaric *Amanita verna, mappa*. It is recommendable, generally speaking, not to use as food fungi of a similar smell.

Mycena alcalina and *Inocybe rimosa* have a distinct odour of lye, whereas *Tricholoma saponaceum* is recognized as edible by its soapy smell.

A repulsive smell is found in *Elaphomyces granulatus, Lepiota Carcharias* and *Scleroderma vulgare*[1]).

W. Brandt[2]) reports on the anatomy and chemistry of the glands of common rue, which are numerous in the mesophyl of the plant. When fully developed, these glands are round or pear-shaped, surrounded by a layer of flat, compact cells, and extend as far as the epidermis of either surface. In the middle of the gland there is a large drop of essential oil, round which there are one or several layers of more or less disorganized cells. The epidermis cells covering the glands are a little below the level of the others, they are flatter than these and conspicuous by their shape and arrangement.

The oil glands of the *Rutaceæ* have attracted attention for a long time already, as well regarding their formation as concerning the secretion of volatile oil in them. An extensive index of all the literature on the formation of oil glands in this family is found in Tschirch's *"Harze und Harzbehälter"*, 2nd. edition, page 1102.

The chief components of the rue oils are methylnonyl and methylheptyl ketones, whereas the corresponding secondary alcohols are present in smaller proportion; besides, there is a mixture of free fatty acids. Young fruits, the glands of which are still growing fast, exhale on being pounded the pure smell of the ketones, but the almost fully-grown smell, besides, disagreeably of sour perspiration. It is therefore natural to presume that in the activity of the glands, in the modification of the oil while the plant is growing, and perhaps also in the act of forming the volatile oil, oxidizing ferments act an important part. Brandt failed to prove it, but it is fairly certain that in the granular parts of the glands of *Ruta graveolens* there are bodies which easily give off oxygen. As these are found in the oil-forming tissue and precisely where the formation of the oil takes place, the view that an oxidation process acts an important part in the synthesis of essential oils gains in probability.

Brandt further reports on the occurrence of bergaptene in the fruits of *Ruta graveolens*. The m. p. was found to be at 187° C. On mixing with pure bergaptene, no lowering of the m. p. took place. Melting with potash led to phloroglucinol. So far, the presence of bergaptene had only been proved in the fruit peels of bergamots[3]) and of *Fagara xanthoxyloides (Rutaceæ)*[4]).

Furthermore, xanthotoxin (m. p. 145° C.) was observed in the fruits of *Ruta chalepensis*, whereas it had previously been known only as a component of *Fagara xanthoxyloides*[4]).

[1]) According to our observations, the latter smells of *iso*nitril. — [2]) *Zur Anatomie und Chemie der Ruta graveolens* (On the anatomy and chemistry of *Ruta graveolens*). Inaugural dissertation, Berlin 1915. — *Arbeiten a. d. pharm. Inst. d. Univ. Berlin* **11** (1914), 82. — [3]) Gildemeister und Hoffmann, *Die ätherischen Öle*, 2nd. ed., vol. III, p. 68; *Report* April **1913**, 149. — [4]) Gildemeister and Hoffmann, *The Volatile Oils*, 2nd. ed., vol. II, p. 632.

Formation of glucosides in germinating seeds.

Already before, G. Ciamician and C. Ravenna[1]) investigated the behaviour of organic compounds, when brought into plants either by introduction into the stem or by absorption through the roots. In either case, there were signs, or even proofs, of the formation of glucosides in the plants if certain aromatic substances had been taken up. It seemed interesting, in consequence, to investigate whether something analogous would happen in seeds. They therefore selected[2]) on the one hand the seeds of Indian corn, wheat, beans, lupines and vetch and, on the other hand, saligenin, benzyl alcohol, quinol, pyrocatechol, gallic acid and tannin. In the grains of Indian corn, as well as in beans, which had been made to germinate on filter paper soaked with a 10 per cent. saligenin solution, the presence of salicin could be proved. A similar experiment, carried out in the dark, showed the same result, so that light is not necessary for the formation of glucosides. When using benzyl alcohol, traces of a glucoside-like compound were obtained, which, on being boiled with hydrochloric acid, was reconverted into benzyl alcohol. It may, therefore, be followed that germinating seeds form glucosides the same as fully-grown plants.

Salinigrin. In the black bark of *Salix discolor*, a glucoside is found, which differs from salicin. It has been called salinigrin and seems to be the glucoside of the *m*-hydroxybenzaldehyde. G. Bargellini and R. de Fazi[3]) have tried to prepare salinigrin synthetically. They obtained, on shaking *m*-hydroxybenzaldehyde in dilute soda lye with an ethereal solution of aceto-bromoglucose, the tetra-acetyl compound of the glucoside of *m*-hydroxybenzaldehyde. On saponification of this body, however, only resinous substances have been obtained so far.

β-Salicylgalactoside. On page 20 of our *Report* of October **1913**, we pointed out already that E. Bourquelot and Hérissey[4]) had succeeded in preparing *β*-salicylglucoside, an isomeride of salicin, biochemically from salicylalcohol and glucose in the presence of emulsin. In the same way, Bourquelot and A. Aubry[5]) obtained *β*-salicylgalactoside by using galactose instead of glucose. The glucoside was obtained in a crystalline state.

The phytochemical reduction of citronellal to citronellol is described on page 120 of this *Report*.

On shading experiments with basil, see page 5 of this *Report*.

As to the constitution of anemonin, see page 134.

Physiological Notes.

Psychological investigations of the sense of smell.

H. Henning has carried out, in the psychological institute of Francfort University, extensive experiments as to the sense of smell. The results of the extraordinarily manysided investigations are a valuable addition to the experiences made so far in

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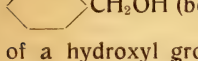
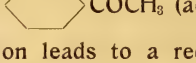
[1]) See *Reports* October **1910**, 171; October **1911**, 125. — [2]) *Atti R. Accad. dei Lincei*, Rome, (5), **25**, I (1916), 3; *Chem. Zentralbl.* **1916**, II. 21. — [3]) *Gazz. chim. ital.* **45** (1915), II, 10; *Chem. Zentralbl.* **1915**, II, 894. — [4]) *Journ. de Pharm. et Chim.* VII. **8** (1913), 49. — [5]) *Ibidem* VII. **13** (1916), 273. — *Compt. rend.* **162** (1916), 610; *Journ. chem. Soc.* **110** (1916), I. 413.

this domain. The corresponding article in the *"Zeitschrift für Psychologie"*[1]) comprises about 100 pages, to which we beg to refer the specialist, as it would lead us too far here to report in full and as it is almost impossible to render adequately a number of important scientific terms which, as the author admits himself, he was obliged to coin for the purpose, owing to the lack of sufficiently expressive words in common parlance. Henning promises additional publications on the same subject, to which specialists may look forward with interest.

R. Marchand[2]) calls attention to some relations between constitution and odour of organic substances. With a view to the preparation of new aromatics, it is of the greatest interest to get to know the action of the single groups, and there has been, in consequence, no scarcity of experiments in order to study their odoriferous influence. The results were rather disappointing, as the so-called odoriferous groups recur in widely different aromatics and there, apparently without any rules, give rise to the most varied odours. When taking into consideration *e. g.* the group $\cdot C\langle^{O}_{H}$, one recognizes that, apparently, it can produce any smell, such as in citral, benzaldehyde, octaldehyde, and phenylacetaldehyde. The odours of these aldehydes do not show the slightest relation to one another. It is almost impossible to establish any rules for the odoriferous action by dividing the bodies into alcohols, aldehydes, ketones, &c. One must, in consequence, come to the conclusion that the influence of said group is quite accidental as regards smell. It is the nature of the nucleus or main group which has determinating influence on the smell. Furthermore, the position of the group concerned in the chief molecule must be taken notice of. How little the group and how much the position produces the smell can best be traced in the benzene derivatives. The group only shades the odour but keeps it in the same class.

The first rule found is that the introduction of an odoriphorous group always leads to the bitter almond class. The group itself only gives variations of one and the same class of odour, so that non-experts always designate them as being like bitter almond, which is the case with ·NO_2 (nitrobenzene), CHO (benzaldehyde),  CH_2OH (benzyl alcohol) and  $COCH_3$ (acetophenone)[3]). The substitution of a hydroxyl group in para position leads to a reduction of the smell or even to inodorousness. If the first group has a mobile atom of hydrogen, the body becomes inodorous on introduction of the hydroxyl group in para position. Such is the case with *p*-hydroxybenzaldehyde, quinol and *p*-hydroxybenzyl alcohol. By fixing the hydrogen in the hydroxyl group, strongly odoriferous bodies are generally formed, such as anisaldehyde (aubépine) from *p*-hydroxybenzaldehyde, methyl quinol from quinol, &c. The same is attained if between the hydrogen atoms in para position a third group is introduced, which does not contain any hydroxyl hydrogen. The insertion of a further hydroxyl group does not interfere with the inodorousness. Protocatechualdehyde (3,4-dihydroxybenzaldehyde) is odourless. If the hydroxyl group in meta position is fixed by means of methyl, vanillin results. Heliotropin, allied in odour with vanillin, proves that the principal matter is not the methoxyl group, but

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[1]) *Zeitschr. f. Psychologie* **73** (1915), 161; **74** (1916), 305; **75** (1916), 177. — [2]) *Deutsche Parf.-Ztg.* **1** (1915), 232, 243, 287. — [3]) We would mention that benzyl alcohol only smells of bitter almonds if it is partly oxidized, *i. e.* if it contains benzaldehyde. Pure benzyl alcohol does not show this odour.

the fixation of the hydrogen. If, in quinol, the second hydrogen atom is likewise fixed, the odour is intensified.

The carboxyl group directly combined with the nucleus is inodorous, but if a group is introduced between it and the nucleus, the body sometimes becomes strongly odoriferous, such as with phenylacetic and cinnamic acids. Aliphatic substances, as is known, likewise smell strongly. It is, therefore, in these cases not the hydroxyl group but the proximity to the nucleus which, acting in a similar way as hydrogen, causes inodorousness.

If the benzene nucleus is ortho-substituted, aromatics are obtained which belong to a distinct class. Even quite different groups produce an odour, which distinctly indicates that they belong to this class; so, according to the author's opinion, *o*-hydroxybenzaldehyde (salicylaldehyde) and *o*-chlorophenol have a similar smell, and that of methyl salicylate (*o*-hydroxymethyl benzoate) would likewise point out the connection of this body with said class. Therefore, wherever the hydroxyl group in para position causes odourlessness, in ortho position it creates a determinate class of odour.

The methoxyl group, found in almost every aromatic, is of great influence.

Marchand resumes his views in the following sentences: —

1. Aromatics are chemical substances which, in the main, contain an oxygen atom as linking atom.
2. A second hydroxyl or carboxyl oxygen atom in the same molecule greatly reduces the smelling power or destroys it altogether.
3. The affinity of two oxygen atoms in the same molecule is neutralized by a CH_3 group in close vicinity, so that their inodorousness is likewise done away with.
4. Strongly smelling bodies contain oxygen as a double-linked atom.
5. The combination of two oxygen atoms, unfavourable for aromatics, is favourable for disinfecting action.

In a treatise on the "Sense of smell and smelling substances in the animal kingdom" G. Rörig[1]) discusses the phenomena in animal life which have direct connection with their sense of smell or their own peculiar odour. It is not always necessary that animals be brought together in large numbers, as *e. g.* in zoological gardens, but very often the presence of one single animal suffices to make its own odour noticeable. So, a good many people smell at once when there is, or has been, a mouse in the room, and to others the smell of dog or a cat, of which some do not notice anything, is repulsive in the highest degree.

The own peculiar smell and the sense of smell are, above all, means for maintaining genus; the former facilitates the meeting of individuals of the same genus and to preserve this, as well as, in special cases, to keep enemies away, whereas the latter has to examine the surrounding medium (air, water), to find food, to secure the return to the abode in case of leaving it temporarily, to discover enemies and, as the own smell, to promote the union of individuals of the same genus. It would be a mistake to declare that those animals smelled the strongest themselves which have the keenest sense of smell. It would be more correct to say that animals with a keen sense of smell make the best use of it in their intercourse. The glands which secrete the smelling substances, by means of which the animals find one another, are frequently situated only in a few parts of the body but are specially suitable for communicating the peculiar smell of the animals to their surroundings. In many cases the feet bear

[1]) *Deutsche Parf.-Ztg.* 2 (1916), 214.

these glands and therefore leave a trail on the ground which is far more lasting than the simple impression of the foot and shows more plainly to what genus the animals belong.

The three principal means by which animal communities are maintained and by which males are sought for, are the senses of sight and smell and the voice. The sense of smell of the insects, which are on so much lower a level than the vertebrates, is developed to such perfection that we are unable to grasp it, especially in the male, whose task it is to search for the female.

Insects smell with their feelers, on which there are, in varying number, small cavities with a sense papilla in the centre, or simply such papillæ, protected by special hairs. Insects with a very strong sense of smell have many such cavities and remarkably big feelers or, at any rate, feelers the surface of which is increased by lamellæ or similar structures. The honey bee, *e. g.*, has from 14000 to 15000 such cavities and about 200 papillæ on each feeler, the male cockchafer 39000, whereas the female only possesses 8000 on every feeler. In certain twilight moths, the surface of the feelers is increased by comb-like structures, and thus achievements are arrived at which one would call exaggerated if they had not been verified thousandfold. So Standfuss caught within 6½ hours 127 males of *Saturnia pavonia* in a neighbourhood where this insect was scarce, by placing a female in a perforated box near the closed window. The following experiment proves that in such a case exclusively the sense of smell is concerned: If the female is covered with a glass dish and then placed near the open window, but the box with sand, on which it had been kept so far, in the middle of the room, the males will flutter past the female and as far as the sand on which it had been before. The males of certain moths, as may here be mentioned, sometimes try to join a female, kept permanently in a room of a house, by passing through the chimney and the fire-place. Such an extraordinary capability of the sense of smell can only be explained, as it is used exclusively for this sole pupose, by that it is specially adjusted to the smell given off by the female and remains more or less unaffected by other smells. At any rate, in this way, insects which live secluded or occur but seldom will find one another with certainty, so that the maintenance of the species is secured.

In a similar way, the sense of smell and the own peculiar smell serve to hold together the communities of many mammals. It can easily be observed, with gregarious animals, that if one has gone away or the whole community has been dispersed, they all unite again within a short time.

To what an extent animals living in the same district are guided by their sense of smell, even if they are not gregarious, is shown by their distinctly recognizable paths in the woods, by means of which they get from the feeding place to the resting place, from the thicket to the meadow, in short, to wherever others of their kind are used to go. Similar paths can be traced on the fields. If *e. g.* field mice have multiplied strongly, so that hundreds of their holes are to be found on a comparatively small surface, all these holes are joined by a network of paths, due to that one mouse always follows the trail of another.

Rörig further calls attention to the remarkable fact that animals which are capable of following a trail are able, when crossing any, to recognize the direction in which man or animal have moved, *i. e.* to the right or to the left. So far, it has not been possible to find a satisfactory solution of this question.

Many animals, which are not gregarious, have the tendency to make their presence known to other members of their species by a more lasting means than the trail, which disappears after some time and is, therefore, rather uncertain. They do this by

depositing their excrements or urine in such places as are frequently visited by their likes. This can be noticed with dogs in the towns as well as with foxes in field and woods.

Pharmacological Notes.

Essential oils as aromatics for cod liver oil emulsions.

G. M. Beringer[1]) examined some essential oils and odoriferous substances with regard to their suitability as aromatics for cod liver oil emulsions. He found that coriander, geranium and aniseed oils, in the proportion of 4:1000, and oil of cardamoms in the proportion of 2:1000, completely mask odour and taste of cod liver oil. The success was less complete with bitter almond, clove and pimento oils (4:1000) as well as with vanillin (1:1000).

The use of aniseed oil against itch is discussed on page 5 of this *Report*.

The treatment of bronchorrhœa and blennorrhœa with eucalyptus oil is spoken of on page 31.

Oil of turpentine as a hæmostatic. Our *Report* of October **1915** (page 71) contains an article on the treatment of wounds with oil of turpentine in the form of a tincture and a serum. From a communication of G. G. Turner[2]) it results that oil of turpentine is an excellent hæmostatic too. A serious hæmorrhage after an operation of the elbow could in no way be stopped until, at last, gauze soaked with oil of turpentine was put on the wound, when the bleeding, which had lasted for a considerable time already, ceased at once. The method is chiefly used in secondary hæmorrhages, but has likewise proved very good in many other cases. Oil of turpentine must be used only after the wound has thoroughly been cleaned. The method is of special value when the origin of the bleeding cannot be traced or it reaches an alarming extent. The oil acts as an antiseptic, as by its action on the living tissues a slimy pus is formed, which facilitates the removal of the gauze after 48 hours. The only drawback is a slight blistering on the skin, which can, however, be avoided through care. The application is not restricted to limbs, as oil of turpentine has proved excellent against bleedings in teeth, but it is not known as yet, in how far it acts when given internally.

The treatment of ankylostomiasis and hook-worm disease with American wormseed oil, and the physiological action of this remedy, have been discussed on page 61 of this *Report*.

Chemical Notes.

In an article, entitled, "Adolf von Baeyer and his influence on the development of the Chemistry of hydroaromatic compounds and terpenes", C. Harries[3]) values the merit of this prominent investigator concerning the chemistry of the terpenes. It was he who furnished the basis for the stereochemical relations of the ring systems, the chemistry of the double bonds and the methodology of the determinations of place in the terpene range.

"It is", says Harries, "Wallach's great merit to have characterized, and traced back to comparatively few main forms, the countless products of different origin. These

[1]) *Americ. Journ. Pharm.* **87** (1915), 115; *Chem. Zentralbl.* **1916**, I. 172. — [2]) *Lancet* **1915**, 226 of July 31st.; *Pharmaceutical Journ.* **95** (1915), 333. — [3]) *Naturwissenschaften* **1915**, number 44.

extensive works of Wallach's go back as far as 1884, when he recognized cineole as an oxygenous derivative of dipentene by transforming it into dipentene tetraiodide and tetrabromide. The endless difficulties which Wallach met with when isolating the terpenes from plant oils and characterizing them, explain why, up to the nineties of last century, so little work was done, comparatively speaking, with a view to ascertain the exact constitution of these compounds. It had been stated with all certainty that terpenes may be converted into cymene (*p*-methyl*iso*propylbenzene) or its derivatives. Numerous intermediate stages were likewise known. It had been shown that pinene from oil of turpentine may be converted, by means of sulphuric acid, into dipentene and further into terpinene, that dipentene is a racemic compound of *d*- and *l*-limonene and that the phellandrene from oil of water fennel may likewise be converted into terpinene. By hydration, an unsaturated alcohol, terpineol, was obtained from dipentene; and a dialcohol, terpin, from limonene. But it had not been ascertained, as yet, where the double bonds were situated and which carbon atom was joined by the hydroxyl in the formation of terpineol and terpin from limonene.

Here, Baeyer found the most suitable sphere where to use the experience gained through the study of hydrated benzene-carboxylic acids and the transformation products of succinylsuccinic acid ester, and so we see how, in his first article, he develops exactly the whole program."

A short characteristic follows of Baeyer's numerous works in the domain of the chemistry of the terpenes and the volatile oils which it would lead us to far to reprint.

Relations between constitution and physical properties of isomeric and homologous hydroaromatic compounds. K. von Auwers who, with his collaborators, repeatedly investigated[1]) the relation between optical behaviour and constitution, has now published a treatise concerning hydroaromatic hydrocarbons, alcohols and ketones, and another on the relation between constitution and physical properties of isomeric and homologous hydroaromatic compounds[2]). The former investigation was carried out conjointly with R. Hinterseber and W. Treppmann. The bodies described are, with a few exceptions, already known, but several of them had, so far, been only examined superficially. Above all, the optical behaviour had to be determined more exactly, as for most substances the index of refraction had been ascertained only for the *D*-line and but isolated indications as to the dispersion were found; in most cases exact determinations of density were missing. K. von Auwers and his collaborators investigated samples of different manufacture or origin of most of the compounds, in order thus to become independant of accidentals in the quality of the preparations as well as in the observations. As to the purity of the substances, the authors believe that the saturated hydrocarbons and ketones examined were absolutely pure. For unsaturated hydrocarbons, there exists the theoretical possibility that isomerides may have been admixed, for in most cases no means is known so far, by which to determine the absolute purity of alkyl*cyclo*hexenes. The conditions are most difficult with alcohols. It is impossible to separate stereoisomeric modifications, if one does not succeed in obtaining them in solid form and purifying them by recrystallization. The number of the possible *cis*- and *trans*-modifications, and further of the optically active or inactive isomerides, rises so quickly with the number of substituents, such as alkyl groups, that even with fairly simple compounds conditions soon become very intricate. No wonder, therefore, that the most contradictory statements are found in literature, *e. g.* regarding the melting points of

[1]) See *e. g. Reports* October **1909**, 173; October **1910**, 164; October **1911**, 122; April **1912**, 158, 168; October **1915**, 62, 76. — [2]) *Liebigs Annalen* **410** (1915), 257, 287.

hydroaromatic alcohols. In addition, these carbinols are often highly hygroscopic and small quantities of moisture may already hinder congealing. In order to dry these alcohols, dry hydrogen had frequently to be passed through them for hours. If the substances were uniformly heated at the same time, the density increased regularly in some cases, and it was not always possible to arrive at any final stage. This was specially noticeable with 1-methyl*cyclo*hexanol-3, when, with the increasing density, the originally normal values of the molecular refraction sank lower and lower. It seems that these alcohols, on being dried sharply and for some considerable time, undergo a chemical change, regarding the nature of which nothing can be said so far. As to the preparation of unsaturated hydrocarbons from these carbinols, the treatment with phosphorus pentoxide is to be recommended for secondary, that with potassium hydrogensulphate, for tertiary alcohols. Sometimes, however, potassium hydrogen sulphate acts polymerizing and should then be replaced by oxalic acid.

The second publication bears the title, "On the Relationship between constitution and physical properties of isomeric and homologous hydroaromatic compounds". The following laws have been established: 1. The boiling point of saturated alcohols and ketones sinks with the approximation of methyl to the hydroxyl and ketone groups, whereas that of singly unsaturated hydrocarbons rises when methyl joins the double bond. The position of the methyl groups to one another only acts a secondary part, in comparison. According to the indications made hitherto, there are no distinct rules recognizable with certainty as to the boiling points of saturated hydrocarbons; this may, however, be due only to the defectiveness of the observations. 2. The density increases, generally speaking, in all the four classes of bodies, as the methyl groups go more closely together in the molecules and these approximate a double bond or a hydroxyl or carbonyl group. 3. Similar relations exist between constitution and refractive index, but they are not so pronounced. 4. The molecular refraction of isomerides of all the four classes is the greater, the farther the side chains are apart and away from either the double bond or the oxygenous component. 5. The molecular dispersion is normal for all the saturated or endocyclically unsaturated compounds, so that it is also the same for the isomerides, within a certain margin. 6. In direct opposition to the rules given are the properties of the 1,1-dimethyl*cyclo*hexanol-4 and the corresponding ketone, for both substances have, in addition to high boiling points (which is according to the rule), a remarkably great density and refractive index, whereas middling or low values would have to be expected. It remains to be ascertained whether compounds with a *gem.*-dialkyl in para position generally make such an exception with regard to their constants. 7. Methene derivatives have lower boiling points and are less dense than isomerides with endocyclic double bonds, but have approximately the same refractive index.

Above rules apply in the first instance to once ond twice methylated compounds. As to the bodies substituted to a higher degree, reliable material is partly wanting and, besides, the differences between the isomerides seem to be somewhat lessened owing to the complicated conditions and the thus created different influences.

In *cyclo*hexanes and *cyclo*hexenes, the entrance of methyl regularly causes the b. p. to rise, although it does not seem to be excluded altogether that in homologues, built up in very dissimilar form, the boiling points may almost coincide or that the higher homologue may boil at a lower temperature. This is often the case in *cyclo*hexanols and *cyclo*hexanones. It is readily understandable that the density of oxygenous substances sinks with the number of methyl groups entered and it is confirmed with regard to hydroaromatic alcohols and ketones. In *cyclo*hexenes, the methyl groups generally

likewise lower the specific gravity, if the substances compared are constructed in an analogous way, but the contrary occurs pretty frequently with homologues of unlike structure. As far as saturated hydrocarbons are concerned, the difference in the densities of the homologues is only small.

No rules can be established concerning the refractive indexes of homologues; here the constitutive influences preponderate completely. The observations already made have been collected by von Auwers, arranged and, to a great extent, calculated again. They had to be supplemented by determinations, meant to serve for checking previous indications, and by examinations of compounds of determinate constitution, which partly had to be prepared specially for the purpose. In order to calculate the refractive indexes for the normal temperature of 20°, the factor 0.00045 for 1° has been used, which is sufficiently accurate for all the cases under consideration. As to the specific gravities, it is not recommendable, however, to avail oneself of either of the most frequently used constant factors of 0.0008 or 0.00093 for 1°, but 1/900 on an average for 1°, as proposed by Roth and Eisenlohr[1]).

We beg to add a list of compounds investigated by the authors, but refrain from entering into details:

	Boiling point	Density	n_D
*cyclo*hexane	80 to 80.2° (749 mm.)	$d_{4^\circ}^{11.2^\circ}$ 0.7869	1.43119 (10.85°)
*cyclo*hexene	83 to 83.5° (760 mm.)	$d_{4^\circ}^{15.6^\circ}$ 0.8143	1.44921 (15.1°)
methene*cyclo*hexane	102.5° (756 mm.)	$d_{4^\circ}^{17.6^\circ}$ 0.8036	1.45092 (17.8°)
1,3-dimethyl*cyclo*hexane	118 to 120°	$d_{4^\circ}^{21.8^\circ}$ 0.7701	1.42398 (22.0°)
1,2-dimethyl*cyclo*hexene-1	—	$d_{4^\circ}^{13.7^\circ}$ 0.8315	1.46178 (13.5°)
1,3-dimethyl*cyclo*hexene-3	124 to 126° (760 mm.)	$d_{4^\circ}^{22.6^\circ}$ 0.7998	1.44533 (22.4°)
1,3-dimethyl*cyclo*hexene-5	126 to 127° (746 mm.)	$d_{4^\circ}^{21.1^\circ}$ 0.797	1.44361 (21.1°)
1,4-dimethyl*cyclo*hexene-1	124 to 126° (751 mm.)	$d_{4^\circ}^{22.4^\circ}$ 0.7985	1.44373 (22°)
ethene*cyclo*hexane	136 to 136.4° (766 mm.)	$d_{4^\circ}^{17.3^\circ}$ 0.8239	1.46389 (17.6°)
1,3,5-trimethyl*cyclo*hexene	139 to 141° (766 mm.)	$d_{4^\circ}^{24.7^\circ}$ 0.7941	1.44378 (24.7°)
1,3-dimethyl-5-methene*cyclo*hexane	135 to 136° (744 mm.)	$d_{4^\circ}^{14.1^\circ}$ 0.7922	1.44628 (14.6°)
*cyclo*hexanol m. p. 23°	66 to 69° (15 mm.)	$d_{4^\circ}^{22.6^\circ}$ 0.9463	1.46560 (22.6°)
1-methyl*cyclo*hexanol-1	56.5° (10 mm.)	$d_{4^\circ}^{24.9^\circ}$ 0.9249	1.45874 (24.65°)
1-methyl*cyclo*hexanol-2	167.4 to 167.6°	$d_{4^\circ}^{13.4^\circ}$ 0.9333	1.46585 (13.4°)
1-methyl*cyclo*hexanol-3	76 to 78° (14 mm.)	$d_{4^\circ}^{24.6^\circ}$ 0.9179	1.45444 (24.3°)
1-methyl*cyclo*hexanol-4	74.7 to 75.2° (12 mm.)	$d_{4^\circ}^{22.5^\circ}$ 0.9183	1.45594 (20.7°)
1,3-dimethyl*cyclo*hexanol-3	79 to 81° (21 mm.)	$d_{4^\circ}^{22.9^\circ}$ 0.9028	1.45414 (22.9°)
1,4-dimethyl*cyclo*hexanol-4	70 to 72° (12 mm.)	$d_{4^\circ}^{23.9^\circ}$ 0.9060	1.45534 (23.9°)
1,3-dimethyl*cyclo*hexanol-5	89° (16 mm.)	$d_{4^\circ}^{18.4^\circ}$ 0.9004	1.45622 (18.4°)
1,3,5-trimethyl*cyclo*hexanol-5	83 to 85° (15 mm.)	$d_{4^\circ}^{24.7^\circ}$ 0.8861	1.45115 (24.7°)
*cyclo*pentanone	130.0 to 130.4°	$d_{4^\circ}^{18.2^\circ}$ 0.9509	1.43757 (17.8°)
*cyclo*hexanone	156.6 to 156.8°	$d_{4^\circ}^{15.6^\circ}$ 0.9501	1.45261 (15.3°)
*cyclo*heptanone	—	$d_{4^\circ}^{21.5^\circ}$ 0.9498	1.46027 (21.9°)
1-methyl*cyclo*hexanone-2	167° (740 mm.)	$d_{4^\circ}^{15.1^\circ}$ 0.9296	1.45049 (14.6°)
1-methyl*cyclo*hexanone-3	60 to 60.2° (15 mm.)	$d_{4^\circ}^{25.15^\circ}$ 0.9139	1.44313 (25.15°)
1-methyl*cyclo*hexanone-4	55.8 to 56.4° (10.5 mm.)	$d_{4^\circ}^{24.4^\circ}$ 0.9119	1.44322 (24.4°)
1,3-dimethyl*cyclo*hexanone-5	70 to 72° (12 mm.)	$d_{4^\circ}^{24.5^\circ}$ 0.8916	1.44102 (24.5°)

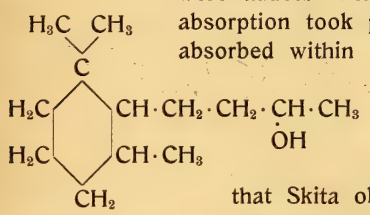
[1]) *Refraktrometrisches Hilfsbuch*, Leipzig 1911, p. 76; *Report* April **1912**, 150.

Investigations of the hydrogenation of unsaturated compounds.

When certain unsaturated aldehydes were hydrogenated, it resulted that only 1 molecule of hydrogen was taken up if the concentration of the platinum was small, whereas 2 molecules of hydrogen were taken up under the influence of the same quantity of platinum, if the concentration was greater. On converting an aromatic substance into a hydroaromatic one by catalytical reduction, groups liable to be easily reduced may be protected by means of derivatives. According to A. Skita[1]), one thus obtains quantitatively hydrocinnamaldehyde on shaking 5 g. of cinnamaldehyde, dissolved in 100 cc. of acetic acid, with colloidal platinum, whereas 5 g. of cinnamaldehyde, dissolved in only 50 cc. of acetic acid, absorb 2 molecules of hydrogen in the presence of the same quantity of colloidal platinum and quantitatively form hydrocinnamyl alcohol. By conducting hydrogen into a solution of 10 g. of cinnamaldehyde in 100 cc. of alcohol, in the presence of 10 cc. of a 1 per cent. palladous chloride solution, 20 cc. of a 2 per cent. gum arabic solution and 30 cc. of water, the cinnamaldehyde absorbs 1 molecule of hydrogen and forms hydrocinnamaldehyde; in addition, a slight amount of cinnamyl alcohol is formed. If 6 g. of cinnamaldehyde, dissolved in 45 cc. of glacial acetic acid, are introduced into a solution of 10 cc. of a 5 per cent. chloroplatinic acid, 25 cc. of a 2 per cent. gum arabic solution and 10 cc. of colloidal platinum, and then saturated with hydrogen unter a pressure of 3 atmospheres, phenylpropyl alcohol (b. p. 235°) and a little propylbenzene are formed. When hydrogen, under a pressure of 4 atmospheres, is conducted into a solution of 5 g. of cinnamaldehyde, 50 cc. of glacial acetic acid, 10 cc. of a 10 per cent. chloroplatinic acid, 30 cc. of a 2 per cent. gum arabic solution and 16 cc. of a solution of 0.003 g of platinum per cc., hexahydrophenylpropyl alcohol results, a colourless liquid of penetrating smell ($d_{20°}$ 0.9358). Besides, insignificant quantities of propylbenzene, hexahydropropylbenzene and phenylpropyl alcohol are formed. By oxidation with sodium bichromate and sulphuric acid, the hexahydrophenylpropyl alcohol is converted into hexahydrophenylpropaldehyde (b. p. 87 to 88° at 15 mm.; semicarbazone, m. p. 128°). If 5 g. of benzaldehyde, dissolved in 35 cc. of alcohol, are added to 25 cc. of a colloidal solution containing 0.08 g. of platinum, and 10 cc. of water, and shaken with hydrogen under a pressure of 2 atmospheres, 1 molecule of hydrogen is absorbed and benzyl alcohol formed. But if 10 g. of benzaldehyde, dissolved in 90 cc. of glacial acetic acid, are mixed with 10 cc. of a 5 per cent. chloroplatinic acid, 25 cc. of a 2 per cent. gum arabic solution and 10 cc. of colloidal platinum are shaken with hydrogen under a pressure of 2 atmospheres, toluene results, the yield being 80 per cent. A solution of 5 g. of benzaldehyde in 50 cc. of glacial acetic acid, 10 g. of a 5 per cent. chloroplatinic acid, 115 cc. of a 2 per cent. gum arabic solution and 8 cc. of colloidal platinum absorbs 560 cc. of hydrogen within 12 hours, when hexahydrotoluene is formed. In order to convert benzaldehyde into hexahydrobenzaldehyde, benzaniline was first prepared and then transformed into benzylaniline in the usual way, with sodium and alcohol. The benzylaniline, dissolved in acetic acid and in the presence of chloroplatinic acid, gum arabic solution and colloidal platinum under a pressure of 4 atmospheres quickly absorbed hydrogen and formed dodekahydrobenzylaniline, which was oxidized with potassium permanganate dissolved in acetone. The oil thus obtained, after having been mixed with concentrated hydrochloric acid, was distilled with steam, when the hexahydrobenzaldehyde passed over (b. p. between 160 and 165°; semicarbazone, m. p. 167°). In a similar way, Skita obtained phenylethyl alcohol, in addition to a little ethylbenzene,

[1]) *Berl. Berichte* 48 (1915), 1486, 1685.

from phenylacetaldehyde. Skita prepared hexahydrophenylethyl alcohol (hexahydro-β-oxyethylbenzene) by conducting hydrogen, under a pressure of 4 atmospheres, into a solution of 3.9 g. of phenylethyl acetate, 30 cc. of glacial acetic acid, 10 cc. of 5 per cent. platino-hydrochloric acid, 10 cc. of colloidal platinum and 5 cc. of a 2 per cent. gum arabic solution. It is a colourless liquid of an agreeable smell, recalling that of otto of roses, and boils between 206 and 209°. The oxidation of this alcohol with potassium bichromate and sulphuric acid in glacial acetic acid leads to hexahydrophenylacetaldehyde, melting between 79 and 80° (10 mm.); semicarbazone, m. p. 153°. α- and β-ionone yield, on hydrogenation, the same hexahydroionone, the new alcohol 1,1,3-trimethyl-2-(hydroxy-3'-butyl)-hexahydrobenzene. For this purpose, 10 g. of α- or β-ionone were dissolved in 50 cc. of glacial acetic acid, when 10 cc. of a 5 per cent. chloroplatinic acid, 20 cc. of a 2 per cent. gum arabic solution and 10 cc. of colloidal platinum were added. Although part of the ionone was not in solution, the absorption took place very quickly. The two first molecules were absorbed within 40 minutes, the third three hours later. From the liquid, a body melting between 142 and 143° (20 mm.) ($d_{20°}$ 0.9126) was isolated, the hexahydroionone. It smells of cedar wood and forms an acetate boiling at 131° (11 mm.). Be it here recalled that Skita obtained, some time ago[1]), dihydroionone and tetrahydroionone through hydrogenation of α- and β-ionones with palladous chloride and hydrogen.



Hexahydroionone.

5 g. of pulegone, dissolved in 40 cc. of glacial acetic acid, were mixed with 10 cc. of a 5 per cent. solution of chloroplatinic acid, 15 cc. of colloidal platinum and 20 cc. of a 2 per cent. gum arabic solution, when under a pressure of 2 atmospheres the first molecule of hydrogen was absorbed after 10 minutes, the second after a further 20 minutes. The liquid then yielded menthol, b. p. 207 to 209°. With an equal concentration of the platinum, it was possible to convert pulegone into menthol likewise in an aqueous-alcoholic solution, when the two molecules of hydrogen were taken up within 60 minutes. On a previous occasion, Skita and H. Ritter[2]) had obtained menthone on reducing pulegone by means of colloidal platinum and hydrogen, whereas menthol was then formed merely as a by-product. They also reduced, at the time, phenylacetaldehyde to phenylethyl alcohol, with the aid of palladium and hydrogen at a pressure of 6 atmospheres.

Preparation of ethers from aldehyde or ketone acetals. By the reaction of organo-magnesium compounds on aldehyde and ketone acetals, A. E. Tschitschibabin and S. A. Jelgasin[3]) obtained, in addition to compounds already known, some ethers distinguished by a characteristic odour. The best yield of ethers was obtained in most cases when organo-magnesium compounds permanently reacted on a considerable excess of acetals. Such conditions are best secured by adding an ethereal solution of organo-magnesium compounds to the acetal, which is being kept at a temperature at which the reaction takes place easily. In a number of experiments with methylal and benzyl-magnesium chloride, carried out by boiling under a reflux condenser as well as by heating in a sealed tube at various temperatures, the following products had formed: toluene, dibenzyl, phenylethyl alcohol (b. p. 212°) or its isomeride and the

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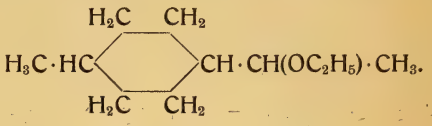
[1]) *Berl. Berichte* **45** (1912), 3312; *Report* April **1913**, 143. — [2]) *Berl. Berichte* **43** (1910), 3393; *Report* April **1911**, 186. — [3]) *Berl. Berichte* **47** (1914), 1843. Consult also *ibidem* 48.

methylether of phenylethyl alcohol (b. p. 189 to 190°). Experiments with ethylal and benzyl-magnesium chloride led to toluene and high boiling hydrocarbons (most likely dibenzylmethane). From *iso*butylal and magnesium benzyl chloride, toluene and dibenzyl resulted, and from magnesium phenyl bromide and acetal, the ethylether of phenylethyl alcohol (b. p. 185 to 187°) was obtained, the yield being 50 per cent. The action of magnesium *iso*butyl bromide on acetal led to the ethylether of methyl*iso*butyl carbinol, unknown before, a liquid of an intense and rather agreeable smell, reminding somewhat of terpineol. B. p. 121 to 122°; $d_{18°}^{18°}$ 0.7612. From magnesium benzyl chloride and acetal, the authors obtained an ether of the formula $C_6H_5 \cdot CH_2 \cdot CH(OC_2H_5) \cdot CH_3$; b. p. 205 to 206°; $d_{18°}^{18°}$ 0.9159. It has an intense smell of nerol. Through the action of *p*-methyl*cyclo*hexyl bromide on acetal, the ether



was formed in addition to methyl*cyclo*hexene and dimethyl*cyclo*hexyl. Its b. p. lies between 197 and 198° (752 mm.); $d_{20°}^{20°}$ 0.8564. Its smell is strong and recalls aniseed. From acetone-acetal and magnesium *iso*butyl bromide, an ether of the formula $(CH_3)_2C(OC_2H_5) \cdot C_4H_9$ resulted; b. p. 140 to 142°; $d_{18°}^{18°}$ 0.7833. It has a strong smell, similar to that of dipentene.

Hydrocarbons.

Isoprene. According to Staudinger and Klever[1]) a good yield is obtained, if either limonene or dipentene, or both mixed, are heated with an indifferent gas to a high temperature under a pressure of 2 mm. They ascribe the rise in yield to the use of dipentene, &c., in a diluted state. The experiments of I. Ostromysslenski[2]) have shown, however, that it is due to the formation of dipentene vapour at a low temperature. When pure limonene is being boiled for a considerable length of time, heavy oils and solid hydrocarbons (polyterpenes) are formed; the reaction is hurried by sodium, but in the presence of from 20 to 50 per cent. of benzene, limonene does not undergo any change, even after having been boiled for some time. On being heated, the limonene is obviously polymerized on the one hand (about between 150 and 250°) and, on the other, depolymerized to isoprene (between 500 and 600°). In order, therefore, to raise the yield of isoprene, the temperature of from 150 to 250° must be avoided as far as possible and the dipentene heated straight off to 500 and 600°. On pyrogenous decomposition of dipentene in naphthalene vapour, only traces of isoprene are formed; a mixture of 75 per cent. of naphthalene and 25 per cent. of dipentene does not yield any isoprene at all. A low concentration of the dipentene vapour may likewise be obtained by subjecting it to a slow pyrogenation (from a dropping-funnel), when extremely small quantities of isoprene result. On the contrary, a very high yield of isoprene is arrived at by subjecting dipentene, &c., to a pyrogenous decomposition in the vapours of a lower-boiling substance. On decomposing limonene in benzene vapour, 70 to 75 per cent. of isoprene are obtained. Instead of benzene, one may use toluene, xylene or light petroleum; the reaction may be carried out under normal pressure. If benzene is used, only small quantities of hydrogen and diphenyl are formed. On decomposing turpentine under the conditions described, in addition to isoprene, gases and hydrocarbons boiling at from 60 to 150° are formed; the latter contain benzene, toluene, xylene and cymene. They all act like benzene in the reaction. Turpentine

[1]) *Berl. Berichte* **44** (1911), 2212; *Report* October **1911**, 127. — [2]) *Journ. russ. phys. chem. Ges.* **47** (1915), 1947; *Chem. Zentralbl.* **1916**, I. 1133.

(the authors here certainly do not mean turpentine, but oil of turpentine) then yields from 25 to 35 per cent. of isoprene.

Mixtures of benzene and French oil of turpentine were decomposed in Andrejew's isoprene lamp, when the yields were as follows: —

pure oil of turpentine							14.6	per cent.	of isoprene
95	per cent.	of turpentine oil	+	5	per cent.	of benzene:	18.8	id.	id.
93	id.	id.	+	7	id.	id. :	19.8	id.	id.
72	id.	id.	+	28	id.	id. :	24.8	id.	id.
50	id.	id.	+	50	id.	id. :	30.6	id.	id.

calculated as percentage of the oil of turpentine used.

The highest yield of isoprene is obtained if the oil of turpentine is not heated before the pyrogenation, by spraying it or dipentene *e. g.* into the space heated to 500 or 600°. Natural myrcene yields on pyrogenation from 60 to 70 per cent. of isoprene.

Some time ago, A. W. Schorger[1]) discovered that the turpentine oil from *Pinus ponderosa*, Laws., chiefly consists of β-pinene. As, according to the German Patent 260934 (U. St. Am. P. 1057680) considerably higher yields of isoprene are supposed to be obtained from β-pinene than from α-pinene, Schorger and R. Sayre[2]) heated ordinary oil of turpentine as well as the variety from *Pinus ponderosa* in Harries' isoprene lamp[3]).

In either case, the principal constituents of the oils (α- and β-pinene) had been increased as far as possible by rectification. No great difference was observed; the yield of isoprene amounted to 8.1 to 10.3 per cent. for oil of turpentine and to 9.4 per cent. for β-pinene from the oil of turpentine from *Pinus ponderosa*. The authors explain the formation of isoprene by an intermediary formation of dipentene according to the scheme: pinene → dipentene → isoprene. In their opinion, the technical use of this reaction for obtaining isoprene would not pay, but as dipentene affords a good yield of isoprene it would be interesting to work out an easy method of converting pinene into dipentene.

The isoprene lamp used by the authors differs somewhat from that described by Harries. Its construction may be clearly understood from the illustration accompanying the treatise.

β-Myrcene. On heating isoprene for 3 to 5 days up to 80 or 90° in a sealed tube, as I. Ostromysslenski and F. Koschelew[4]) discovered, a myrcene-like hydrocarbon is formed, for which they give the formula $CH_2:CH\cdot C(CH_3):CH\cdot CH_2\cdot C(CH_3):CH_2$ and which they call β-myrcene. B. p. 63 to 63.5° (20 mm.); 58° (13 mm.). It is a colourless, readily mobile liquid of myrcene-like smell that irritates the mucous membranes of the nose. The action of sulphuric acid leads, after 2 to 5 days, to an amorphous product. When heated with sodium and benzoyl peroxide, or when acted upon by sodium and barium peroxide, β-myrcene is transformed into isoprene caoutchouc. β-Myrcene is to be considered as an intermediate product of the polymerization of isoprene to caoutchouc. The endeavours to prepare β-myrcene by dehydration of terpene alcohols, such as geraniol, linalool, &c., gave no result.

The polymerization of β-myrcene is perhaps the only synthesis of natural caoutchouc. The identity of the caoutchouc from β-myrcene with the natural Para caoutchouc is shown by the position of the elasticity point and fatal temperature; besides, the temperature curves for viscosity, surface tension and density are analogous for both kinds of caoutchouc. It may be presumed that the synthesis of caoutchouc in tropical plants passes likewise through the stage of β-myrcene or myrcene-like hydrocarbons.

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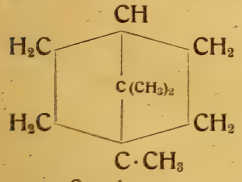
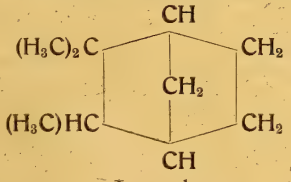
[1]) See *Report* April **1913**, 101. — [2]) *Journ. Ind. Eng. Chemistry* **7** (1915), 924. — [3]) See *Report* October **1911**, 127. — [4]) *Journ. russ. phys. chem. Ges.* **47** (1915), 1928, 1941; *Chem. Zentralbl.* **1916**, I. 1068, 1136.

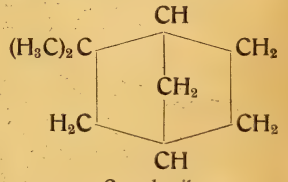
Camphane, camphenilane, iso*camphane.* Together with M. K. Dobrowolskaja, M. P. Oparina, L. N. Abakumowskaja and A. M. Chuchrikowa, S. S. Nametkin[1]) investigated some reactions of the hydrocarbons camphane, camphenilane and *iso*camphane. All three contain the identical bicyclic system and differ only by the numbers and positions of the methyl groups. They are nitrated by dilute nitric acid (d 1.075) only at about 140°, in which behaviour they show analogy with the more constant hydrocarbons of the paraffin series. In the main, secondary nitro-compounds are formed; tertiary nitro-compounds were not obtained. The nitration of camphane (dihydrocamphene) had already previously been carried out by M. Konowalow and S. Kikina[2]). The camphane they used, however, was not pure; it melted between 144 and 152°. Nametkin, therefore, nitrated absolutely pure camphane, prepared from camphylidenehydrazine according to Kishner's process[3]); it melted between 157 and 158°. On being heated for 30 hours in a sealed tube with nitric acid (d 1.075) up to 145/150°, it formed two nitro-compounds; the α-nitrocamphane (m. p. 128 to 130°) and the isomeric α'-nitrocamphane (m. p. 146 to 147°). Both products are not volatile at ordinary temperature and resemble camphor in appearance and smell. On being oxidized with a 2 per cent. potassium permanganate solution at 0°, they both yielded *i*-camphor. In addition to the two nitro-compounds, *i*-camphoric acid had been formed.

It might reasonably be expected that on nitration of *iso*camphane the hitherto unknown bibasic *iso*camphocamphoric acid would be formed, in addition to nitro-derivatives; however, no trace of such an acid was to be detected. But it may be obtained by oxidation of the ketones derived from the nitro-compounds. When nitric acid acts on *iso*camphane, ω-nitrocamphene[4]) and a mixture of secondary nitro-compounds, $C_{10}H_{17}\cdot NO_2$ (m. p. 48 to 49°), of butter-like consistency, are formed. On oxidation with alkaline potassium permanganate solution at 0°, β-*iso*camphone, $C_{10}H_{16}O$ (m. p. 91 to 92°) and β'-*iso*camphone (m. p. 63 to 64°) form from the nitro-compounds. Both ketones are very volatile and their smell reminds of camphor. Further oxidation leads to *iso*camphocamphoric acid (4,4,5-trimethyl*cyclo*pentane-1,2-dicarboxylic acid), $C_{10}H_{16}O_4$.

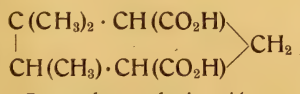
By the action of solid potassium hydroxide on camphenilonehydrazone (m. p. 29 to 31°), Nametkin obtained camphenilane, C_9H_{16}, a hitherto unknown hydrocarbon; m. p. 15 to 16°; b. p. 142.5° (753 mm.); $d_{4^\circ}^{20^\circ}$ 0.8547; n_{D20° 1.4555. The nitration with nitric acid (d 1.075) in a sealed tube led to β-nitrocamphenilane, $C_9H_{15}\cdot NO_2$ (m. p. 18 to 20°), β-*iso*camphenilone, $C_9H_{14}O$ (m. p. 63 to 65°) and 4,4-dimethyl*cyclo*pentane-1,3-dicarboxylic acid, which the authors call *apo*fenchocamphoric acid. The acid forms

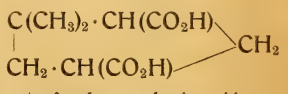

Camphane.


*Iso*camphane.


Camphenilane.

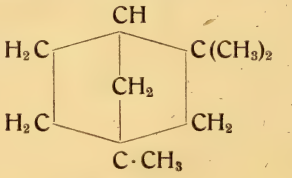
quantitatively on oxidation of β-*iso*camphenilone. This ketone is highly volatile and has a feeble smell recalling that of camphor.


*Iso*camphocamphoric acid.

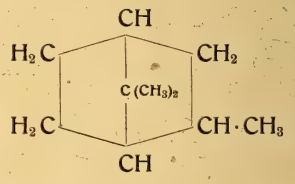

*Apo*fenchocamphoric acid.

[1]) *Journ. Russ. phys. chem. Soc.* **47** (1915), 405, 409, 414, 425; *Journ. chem. Soc.* **108** (1915), 698/701. — *Chem. Zentralbl.* **1916**, I. 884/886. — [2]) *Journ. russ. phys. chem. Ges.* **34** (1903), 935; *Chem. Zentralbl.* **1903**, I. 513. — [3]) See *Report* April **1912**, 195. — [4]) See *Report* October **1913**, 133.

Fenchane and iso*bornylane.* S. Nametkin[1]) investigated on the one hand the fenchane prepared by Kishner and Proskurjakow[2]) through boiling fenchylidenehydrazine with solid potassium hydroxide and, on the other, fenchane obtained by Wolff[3]) on heating fenchonehydrazine with sodium ethylate, and found that both bodies were identical. The fenchane prepared according to Kishner yielded on nitration a secondary nitro-compound and a ketone; no tertiary nitro-compound could be obtained. Nitric acid acts simultaneously on both rings of the fenchane molecule, so that a nitro-compound corresponding to fenchone and another, corresponding to *iso*fenchone, are obtained. The formation of *iso*fenchone and fenchone through the action of nitric acid on fenchane affords the conclusive proof of the identity of the bicyclic systems in Kishner's fenchane, natural fenchone and Bertram and Helle's *iso*fenchone[4]). The nitration of fenchane led to an acid, which is identical with *iso*fenchocamphoric acid. The fenchane described by Zelinski[5]) is of quite different structure. It yields on nitration a tertiary nitro-compound and *apo*camphoric acid, for which reason the author takes it to be a hydrocarbon of the formula II and calls it *iso*bornylane. It boils between 163.5 and 164.5° (753 mm.); $d_{4^\circ}^{20^\circ}$ 0.8579. There is no reaction with permanganate and dilute nitric acid, but it is attacked by fuming nitric acid.



(I) Fenchane.



(II) *Iso*bornylane.

Pinene. In two articles on the chemistry and the therapeutical use of pinene ozonides, J. E. Blomén[6]) gives a short review of all the publications on pinene ozonide and allied bodies, without adding anything new, so that we need not enter into detail.

Limonene. Some years ago, H. Neresheimer[7]) described limonene diozonide and showed that, on oxidation with chromic acid and glacial acetic acid, it passes into an acid, which he considered to be diacetylvaleric acid. That this is correct, is evidenced by a publication of C. Harries and H. Adam[8]). They treated limonene in glacial acetic acid with concentrated ozone up to saturation and kept the solution for two days, gradually adding chromic acid in glacial acetic acid. After the glacial acetic acid had been evaporated *in vacuo* as far as possible, the syrupy residue was extracted with ether and the ether then removed. A perfectly clear, thick syrup remained, from which, on esterification with methyl alcoholic hydrogen chloride, a product was obtained, composed most likely of a mixture of methyl diacetylvalerate and its dehydration product. As a diketo acid with the ketone carbonyles in 2.6 position, the acid ought to be susceptible of splitting off water and consequent ring formation. On being heated with alkali, it likewise splits off water, but it has been impossible so far to determine in what way; theoretically, there are two possibilities.

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[1]) *Journ. Russ. phys. chem. Soc.* **47** (1915), 1590; *Journ. Soc. chem. Industry* **35** (1916), 380. — *Chem. Zentralbl.* **1916**, II. 253. — [2]) See *Report* April **1912**, 195. — [3]) *Liebigs Annalen* **394** (1912), 86; *Report* April **1913**, 139. — [4]) See *Report* April **1900**, 55. — [5]) *Journ. russ. phys. chem. Ges.* **36** (1904), 770. — [6]) *Journ. Americ. chem. Soc.* **87** (1915), 199, 398. See *Report* October **1915**, 71. — [7]) Inaugural dissertation, Kiel 1907. — C. Harries, *Untersuchungen über das Ozon und seine Einwirkung auf organische Verbindungen*, Berlin 1916, p. 443. — [8]) *Berl. Berichte* **49** (1916), 1034.

The methyl ester of the anhydride yields a semicarbazone melting between 173 and 174°, a phenylhydrazone melting at 135° and a *p*-nitrophenylhydrazone melting at 173°.

On splitting limonene diozonide with N/ potash lye, a neutral oil results, which is easily volatile with steam, possesses an agreeable, camphor-like smell, but has not been closely investigated as yet.

α-Terpinene. In a treatise on dialkyl*cyclo*hexadienes and their carboxylic acids, K. von Auwers and R. Hinterseber[1]) describe among other matter the preparation of α-terpinene (1-methyl-4-*iso*propyl*cyclo*hexadiene-1,3) from 1-methyl-4-*iso*propyl*cyclo*hexadiene-1,3-one-2 by boiling it with alcoholic potash lye. The constants of this preparation have already previously been communicated by W. A. Roth and K. von Auwers[2]): b. p. 65.4 to 66° (13.5 mm.); $d^{18.9°}_{4°}$ 0.8353; $n_{D18.9°}$ 1.47942. This synthetic terpinene was oxidized by treating it for three hours with ozone in glacial acetic acid. After the ozonides had been decomposed, the mixture was first driven over *in vacuo* and then treated with steam. The oil obtained from the distillate proved to be identical with α,α-dimethylacetonylacetone (semicarbazone, m. p. 200°). The oxidation into this ketone proves that the hydrocarbon is identical with α-terpinene, or at least contains this substance as essential component. The constant b. p. indicates that it is present in a very pure state.

As to the rotatory power of some derivatives of β-phellandrene, see page 7.

Alcohols.

*Allyl*iso*allylcarbinol.* In a communication on Wagner-Saytzeff's reaction with open-chain aldehydes, C. J. Enklaar[3]) describes the preparation of allyl*iso*allylcarbinol from crotonaldehyde. As this reaction may, perhaps, be applied to aldehydes of the terpene series, we are going to discuss it here briefly. The author gradually, and under cooling, added a solution of allyl bromide and crotonaldehyde in an equal volume of ether to zinc wool in a flask with reflux condenser. In order to start the reaction, a little heating was required and, finally, it was necessary to heat for some time on a water-bath. The mixture was then poured into water, the zinc hydroxide dissolved by adding sulphuric acid and the acid liquid treated with ether. The allyl*iso*allylcarbinol, $C_7H_{12}O$, boiled between 156 and 156.7° at 765 mm.; $d^{14.8°}_{4°}$ 0.8668; $n_{D13.7°}$ 1.45527. On being heated with potassium bisulphate, the alcohol readily splits off water.

Bupleurol glycol. With the aid of sodium and alcohol, V. Longinow[4]) reduced the ethyl 6-methylheptane-1,3,3-tricarboxylate to the glycol 7-methyl-3-hydroxymethyl-octane-1-ol (*β-iso*hexyltetramethylene glycol), $CH_3 \cdot \underset{\displaystyle CH_3}{\underset{|}{CH}} \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot \underset{\displaystyle CH_2OH}{\underset{|}{CH}} \cdot CH_2 \cdot CH_2OH$.
This glycol may be looked upon as a derivative of bupleurol[5]), for which reason Longinow calls it bupleurol glycol, in analogy with citronellol glycol. It is a colourless liquid boiling at 160° (9 mm.); $d^{20°}_{4°}$ 0.9277; $n_{D20°}$ 1.4555. The diacetyl compound boils between 151 and 152° (9 mm.); $d^{20°}_{4°}$ 0.9660; $n_{D20°}$ 1.4369. On being heated with sulphuric acid of 60 per cent. in excess, the glycol is transformed into the corresponding oxide;

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[1]) *Berl. Berichte* **48** (1915), 1357. — [2]) *Liebigs Annalen* **47** (1915), 157. As to the preparation of α-terpinene from *o*-cresol, see K. von Auwers and F. von der Heyden, *Berl. Berichte* **42** (1909), 2420; *Report* October **1909**, 172. — [3]) *Berl. Berichte* **49** (1916), 211. — [4]) *Journ. russ. phys. chem. Ges.* **47** (1915), 1132; *Journ. chem. Soc.* **108** (1915), I. 935. — *Chem. Zentralbl.* **1916**, I. 1054. — [5]) See *Report* October **1913**, 28.

b. p. 204° (748 mm.); $d_{4^\circ}^{20^\circ}$ 0.8562; n_{D20° 1.4360. The oxide is a colourless, mobile liquid, the smell of which recalls that of lemon oil.

Alkyl menthols and menthyl esters. A fairly long time ago, A. Haller[1]) showed that through the action of sodium amide on menthone, dissolved in ether, ammonia and the sodium derivative of menthone result and that the latter may be converted into alkyl menthones by the aid of alkyl iodides. The reduction of the menthone homologues, obtained in this way, has now been described by E. Bœdtker[2]); it easily takes place when the ketones in moist ether are treated with sodium. The formation of the alkyl menthones does not always run smoothly and is specially unsatisfactory if high-molecular alkyl groups are introduced. The yield depends upon the quality of the sodium amide; besides, the alkyl halogenide partly interchanges with the sodium amide, when the alkyl menthone acts as solvent. This by-reaction cannot be prevented in any way. From 100 g. of lævorotatory menthone and 100 g. of *iso*propyl iodide, only a few drops of the supposed-to-be *iso*propylmenthone were obtained; b. p. about 130° at 20 mm. About 10 g. of *n*-propylmenthone formed from 50 g. of menthone and *n*-propyl bromide. The yield of *iso*butylmenthone was about 15 g., that of *iso*amylmenthone (b. p. 135 to 140° at 11 mm.; n_{D21° 1.4619) about 10 g. from 50 g. of menthone. Methylmenthone (b. p. 105° at 17 mm.; d_{D20° 1.4610) and ethylmenthone (b. p. 110° at 12 mm.; n_{D21° 1.4646) were obtained in fairly satisfactory quantities. Bœdtker obtained benzylmenthone from benzyl chloride and menthone; b. p. 177° (8 mm.); $d_{4^\circ}^{18^\circ}$ 0.9979; $[\alpha]_{D23^\circ}$ + 23° 4′; n_{D19° 1.5232. The properties of the menthol homologues, obtained by reduction of the alkyl menthones, and their esters are shown in the following tables: —

Alkyl menthols and esters.

	B. p.	$d_{4^\circ}^{18^\circ}$	Optical rotation	n_{D20°
Methylmenthol	129 to 130° (32 mm.)	0.9124	$[\alpha]_{D21^\circ}$ — 2° 26′	1.4692
Methylmenthyl acetate .	125° (17 mm.)	0.9313	$[\alpha]_{D22^\circ}$ — 18° 7′	1.4578
Ethylmenthol	124° (13 mm.)	0.9246	$[\alpha]_{D22^\circ}$ + 4° 55′	1.4769
Ethylmenthyl acetate . .	131 to 132° (14 mm.)	0.9366	$[\alpha]_{D21^\circ}$ — 6° 6′	1.4636
n-Propylmenthol	141 to 145° (27 mm.)	0.9075	$[\alpha]_{D22^\circ}$ + 29° 7′	1.4675
n-Propylmenthyl acetate	152° (30 mm.)	0.9515	$[\alpha]_{D22^\circ}$ — 8° 58′	1.4741 (19°)
*Iso*amylmenthol	150° (23 mm.)	0.8985	$[\alpha]_{D22^\circ}$ + 33° 44′	1.4661
Benzylmenthol[3])	203 to 205° (24 mm.)	$d_{4^\circ}^{20^\circ}$ 0.9819	$[\alpha]_{D20^\circ}$ — 43° 19′	1.5257

Action of esters on magnesium alkyl iodides. On repeating former experiments, G. Stadnikow[4]) found that, at room temperature, the action of magnesium benzhydryl iodide on ethyl acetate consists only in that ethyl is replaced by benzhydryl. In the heat, however, benzhydrol ether is formed. By heating magnesium menthyl iodide in absolute ether with ethyl acetate, menthyl acetate results (b. p. 113° at 19 mm.). If ethyl propionate is used, menthyl propionate (b. p. 122 to 123° at 18 mm.) forms in a similar way. Menthyl benzoate is obtained by heating 0.2 molecule of magnesium menthyl iodide in absolute ether with 30 g. of ethyl benzoate; m. p. 54.5 to 55°, b. p. 191 to 192° at 18 mm. Through the action of ethyl acetate on the magnesium terpinyl iodide, a hydrocarbon of the formula $C_{10}H_{16}$ is obtained (b. p. 182 to 184° at 760 mm.).

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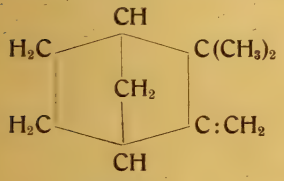
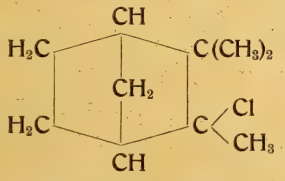
[1]) *Compt. rend.* **138** (1904), 1139; *Report* October **1904**, 125. — [2]) *Bull. Soc. chim.* IV. **17** (1915), 360. — [3]) See Wallach, *Liebigs Annalen* **305** (1899), 263. — F. W. Semmler, *Berl. Berichte* **37** (1904), 236. — [4]) *Journ. russ. phys. chem. Ges.* **47** (1915), 1113; *Chem. Zentralbl.* **1916**, I. 1067.

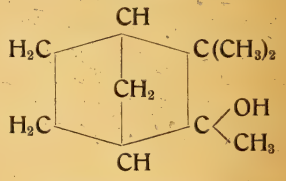
Methylcamphenilol and camphene hydrate. Four isomeric bicyclic alcohols; *viz.*, borneol, *iso*borneol, methylcamphenilol and camphene hydrate, are derived from camphor or the genetically closely related camphene. Methylcamphenilol was first prepared by Tschugaeff and investigated by Moycho and Zienkowski[1]), whereas camphene hydrate was discovered by Aschan[2]). The isomeric relations of methylcamphenilol and camphene hydrate have now been explained by Aschan[3]). These alcohols are geometrically isomeric bodies in the same proportion as borneol and *iso*borneol. Methylcamphenilol results through the action of magnesium methyl iodide on camphenilone, where no transposition is to be supposed. As the constitution of camphenilone is established, to methylcamphenilol the structure given in the formula hereafter would be due. Camphene hydrate forms already at 60° through the action of milk of lime on camphene hydrochloride. When camphene, which contrary to former suppositions is uniform[4]), takes up hydrogen chloride, no transposition takes place. Aschan already previously succeeded in proving this, by transforming a dextrorotatory camphene first into its lævorotatory hydrochloride and then through stirring with alkali into a feebly rotatory camphene hydrate, from which he recovered the camphene, possessing the original rotation, by slightly splitting off water. Furthermore, a camphene hydrochloride of unaltered rotation was recovered, if it was first transformed into camphene hydrate and regenerated with the aid of hydrogen chloride. Hence it is evident that camphene hydrate forms without any transposition of the original camphene skeleton and therefore is a true derivative of camphene. Starting from Wagner's camphene formula,



Camphene.



Camphene hydrochloride.

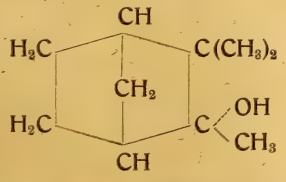


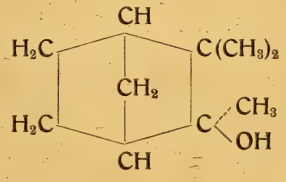
Camphene hydrate.

one arrives at the structure of the camphene hydrochloride as well as of the hydrate. The formula for the latter coincides in structure with that of methylcamphenilol. The two bodies are not identical, however, for they differ in their melting points, their boiling points and in the boiling points of their phenylurethanes, as shown hereafter:

Methylcamphenilol	m. p. 117 to 118°, b. p. 204 to 206°
Camphene hydrate	m. p. 150 to 151°, b. p. 206 to 207,5°
Methylcamphenilol phenylurethane	m. p. 126°
Camphene hydrate phenylurethane	m. p. 89°.

In consequence, it must be a case of stereometric isomerism, as expressed by the formulas





Methylcamphenilol and camphene hydrate.

[1]) See *Report* October **1904**, 111; April **1905**, 91; October **1905**, 104. — [2]) See *Report* October **1911**, 132. — [3]) *Liebigs Annalen* **410** (1915), 222. — [4]) See A. Hesse, *Berl. Berichte* **39** (1906), 1127; *Report* October **1906**, 113.

The structural equality is reflected also in the very similar, in many cases even absolutely identical, behaviour of the corresponding alcohols. They both, *e. g.*, readily form *iso*bornyl acetate in addition to camphene on being heated with dilute sulphuric acid and glacial acetic acid.

Aschan proved that camphene hydrochloride (from camphene in absolute ether on introducing hydrogen chloride), bornyl chloride and *iso*bornyl chloride (from borneol or *iso*borneol, respectively, in light petroleum with phosphorus pentachloride) yield the identical camphene hydrate. As no transposition need be suspected, owing to the mild action of the milk of lime, he thinks that the chlorides in question, *viz.*, camphene hydrochloride, bornyl chloride and *iso*bornyl chloride are likewise identical[1]).

On being boiled with acetic anhydride, camphene hydrate is partly converted into the acetate, boiling between 103 and 105° (14 mm.); $d_{15°}$ 0.9852. Methylcamphenilol forms an acetate boiling between 100 and 102° (11 mm.); $d^{18°}_{4°}$ 1.003; $[\alpha]_D + 18.9°$. While methylcamphenilol is but slightly attacked by boiling glacial acetic acid, camphene hydrate is almost entirely converted into camphene.

On *iso*pulegolphosphonic acid, see page 121 of this *Report*.

Aldehydes.

Phytochemical reduction of citronellal to citronellol.

In former *Reports*, we have discussed already C. Neuberg and his collaborators' publications on the phytochemical reduction of aldehydes to alcohols with the aid of yeast[2]). Neuberg's latest works have been compiled together with E. Schwenk, P. Mayer and M. Ringer[3]). They refer to the reduction of glycolaldehyde to ethyleneglycol, the transformation of ethyl disulphide into ethylmercaptane, that of citronellal into citronellol, the succinic acid fermentation of the α-ketoglutaric acid and the formation of succinic acid from decaying α-ketoglutaric acids.

In order to reduce citronellal, Neuberg and Mayer filled four 5 litre bottles with 250 g. of cane sugar, 2500 cc. of water of 40° and 250 g. of yeast *(Unterhefe K)*. As soon as the fermentation was vivid, 12 cc. of *d*-citronellal, dissolved in 13 cc. of absolute alcohol, were added to each bottle. After vigorous shaking, the fermentation soon stopped but started again after 10 minutes. As the citronellal floats on the surface, the shaking must be repeated frequently. All the four bottles were at first kept at 30° for twelve hours and then at room temperature during the night. The fermentation remained feeble, although the bottles were afterwards placed in an incubator (37°), and it was, therefore, roused by adding another 150 g. of cane sugar and 150 g. of yeast *(Hefe K)*. A very slow fermentation resulted, but it extended over a fortnight. The content of the bottles, which had been closed with cotton wool stoppers, was vigorously shaken at least three times daily, when the whole incubator filled with the typical rose odour. After 15 days, the whole content of the four bottles, which had remained absolutely sterile, was distilled with steam and the distillate treated with ether. The residue of the extraction was treated with sodium hydrogen sulphite solution, in order to remove the possibly present citronellal, and then fractionated *in vacuo*. The *d*-citronellol thus obtained boiled between 107 and 110° (11 mm.); $[\alpha]_{D16°} + 4.32°$. The silver salt of the ester of the citronellyl phthalic acid melted at 123°.

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[1]) See A. Hesse, *Berl. Berichte* **39** (1906), 1127; *Report* October **1906**, 113. — [2]) See *Reports* April **1914**, 128; April **1915**, 91; October **1915**, 82. — [3]) *Biochem. Zeitschr.* **71** (1915), 114, 117, 174, 226, 237.

The formation of dihydrocitronellol could not be observed in this reduction, and it was likewise impossible to reduce phytochemically the double bond ·CH:CH· in previous experiments with allyl alcohol and cinnamic acid. The yield of citronellol amounted in the best case to 59.4 per cent. of the theoretically possible quantity. This transformation of citronellal into citronellol by means of a vegetable organism is, the authors think, interesting not only for plant physiologists but likewise for the chemistry of aromatics. They take it that phytochemical reductions contribute in part to the development of the "bouquet".

A good many years ago, F. D. Dodge[1]), when treating citronellal in moist ethereal solution with phosphorus pentoxide, obtained a compound which he called citronellal phosphoric acid. On discussing this body in his book *"Die ätherischen Öle"* (vol. I, page 614, Leipzig 1906) F. W. Semmler expresses the opinion that the citronellal phosphoric acid really is an *iso*pulegol derivative, for the reactions of the aldehyde group have disappeared. Dodge[2]), in the meantime, has come to the same conclusion, for in a recently appeared publication he proposes for the citronellal phosphoric acid the name of *iso*pulegol phosphonic acid. It is a strong monobasic acid and affords a series of well defined salts which, generally speaking, crystallize easily. It is sparingly soluble in water, but easily in alcohol and chloroform; m. p. 181 to 182°. At a comparatively low temperature, the sodium salt decomposes, forming *iso*pulegol, which was characterized by oxidation to *iso*pulegone; semicarbazone, m. p. about 171°. The acid is not saponifiable with either hot alcoholic potash lye or hot dilute suphuric acid, which indicates that the PO_3 group is combined directly with a carbon atom.

Normal phosphonic acids are dibasic, whereas the *iso*pulegol phosphonic acid is monobasic. It was impossible to obtain a di-potassium salt. The ready formation of *iso*pulegol on dry distillation points to the presence of a secondary hydroxyl group in the acid; on the other hand, the acid cannot be acetylated or oxidized with either chromic acid or dilute potassium permanganate solution, so that the presence of a hydroxyl group (except a tertiary one) seems to be excluded. There cannot be any carbonyl group either in the molecule, for the acid neither forms an oxime nor a phenylhydrazone. Although *iso*pulegol shows the behaviour of an unsaturated secondary alcohol, the *iso*pulegol phosphonic acid appears as a saturated compound. The solution of its sodium salt does not discolour bromine water. The position of the phosphonic group is not yet known.

As may be seen, the structure of the *iso*pulegol phosphonic acid is still rather uncertain, and we think it questionable whether we have really to deal with an *iso*pulegol derivative at all.

In any case, the *iso*pulegol phosphonic acid is a characteristic derivative of citronellal and may possibly be used as a proof of its presence. Dodge tried to prove the presence of citronellal as *iso*pulegol phosphonic acid in normal and terpeneless lemon oils, but without result, from which he deduces that the content of citronellal in lemon oil is but inconsiderable.

The transformation of anisaldehyde into anisic acid with the aid of persulphate has been discussed on page 79 of this *Report*.

o-*Vanillin*. E. Rupp and K. Linck[3]) prepared a series of derivatives of *o*-vanillin, which had partly been described already some years ago by Noelting[4]). However, the

[1]) *Americ. chem. Journ.* **12** (1890), 553. — [2]) *Journ. Americ. chem. Soc.* **37** (1915), 2756. — [3]) *Arch. der Pharm.* **253** (1915), 33. — [4]) *Chem. Zentralbl.* **1910**, I. 1880; *Report* October **1910**, 195.

formation *e. g.* of nitrohydroxymethoxybenzaldehyde (m. p. 142°) from a solution of *o*-vanillin in glacial acetic acid on adding nitric acid is something new. Monobromohydroxymethoxybenzaldehyde (m. p. 127°) forms on brominating the aldehyde in glacial acetic acid. The 2,3-hydroxymethoxybenzaldehyde (*o*-vanillin) is fairly stable with regard to oxidizing substances; the atmospherical air leaves it unchanged and chemical reagents have either no influence or act only on the phenolic hydroxyl group. After having blocked up the hydroxyl group, one easily arrives at the 2,3-hydroxymethoxybenzoic acid (m. p. 148°), which corresponds to the aldehyde, by oxidizing the benzenesulphonated aldehyde, after addition of magnesium sulphate, with a 3 per cent. solution of potassium permanganate. If *o*-vanillin is melted with potassium hydroxide, one arrives at 2,3-hydroxymethoxybenzoic acid, pyrocatechol-*o*-carboxylic acid and pyrocatechol, according to temperature. If *o*-vanillin is subjected to Perkin's reaction, the chief product resulting is the lactone of a 2-hydroxy-3-methoxy-β-phenylacrylic acid.

W. Mosimann and J. Tambor[1]) describe further derivatives of *o*-vanillin. They mention *e. g.* the preparation of methyl carbonato-*o*-vanillin (m. p. 59°) by adding methylchloroformate, and then some hydrochloric acid, to a well cooled solution of *o*-vanillin in soda lye. Furthermore, the preparation of *o*-homoveratrole, 2,3-dimethoxy-1-ethylbenzene, 2,3-dihydroxy-1-ethylbenzene, *o*-veratric acid, 7-hydroxycoumaranone and other bodies is described, which are of little interest for our special domain.

Derivatives of methylvanillin. Independent of Fritsch[2]), B. L. Vanzetti[3]) prepared veratril and veratroin, which are analogous compounds as benzil and benzoin, by condensing methylvanillin. Like Fritsch, he found that veratroin cannot be obtained in a crystalline state.

On melting veratril with potassium hydroxide, in addition to a little veratrilic acid, chiefly veratric acid is formed and a resin, which is most likely analogous to the resin formed on heating benzilic acid.

Ketones.

Menthone. M. Zajcev[4]) reports on some derivatives of menthone. On being treated with allyl iodide and zinc, *l*-menthone ($[\alpha]_D - 27.46°$), which had beed obtained by oxidizing menthol, yielded 3-allylmenthanol (b. p. 125 to 129° at 18 mm.); $d_{4°}^{20°}$ 0.9058; $[\alpha]_D - 3.09°$. The same alcohol resulted from *d*-menthone: b. p. 121 to 124° (14 mm.); $d_{4°}^{20°}$ 0.9061; $[\alpha]_D - 2.88°$. The saturation of these alcohols with hydrochloric acid in the cold, led to the corresponding chlorides, which are transparent liquids boiling under reduced pressure without decomposing. Treatment of the chlorides with silver or nickel carbonates yields 3-allyl-Δ^3-menthene (b. p. 214 to 217° at ordinary pressure and 97 to 100° at 17 mm.); $d_{4°}^{20°}$ 0.8551; $[\alpha]_D + 45.06$ and $+ 50.86°$. On oxidation with potassium permanganate in neutral solution, this hydrocarbon formed a polyhydric alcohol, acetone, acetic, *iso*butyric and β-methyladipic acids. 3-Allylmenthanol, on being oxidized with potassium bichromate and sulphuric acid, yields acetone, acetic, *iso*butyric and β-methyladipic acids, whereas 3-methyl-3-allyl*cyclo*hexanol affords acetic and methyladipic acids.

1-Methyl-3-allyl-Δ^3-*cyclo*hexene is obtained by converting the inactive 3-methyl-1-allyl*cyclo*hexanol into the corresponding chloride and treating this with carbonate of

[1]) *Berl. Berichte* **49** (1916), 1261. — [2]) *Liebigs Annalen* **329** (1903), 37. — [3]) *Atti R. Accad. dei Lincei, Roma* (5), **24**, II (1915), 467; *Chem. Zentralbl.* **1916**, I. 1143. — [4]) *Journ. Russ. phys. chem. Soc.* **47** (1915), 2127; *Journ. chem. Soc.* **110** (1916), I. 267.

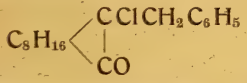
silver. It boils between 171 and 173°; $d_{4^\circ}^{20^\circ}$ 0.8361; $[\alpha]_D + 52.84^\circ$. On oxidation with permanganate, a polyhydric alcohol and β-methyladipic acid result.

When above alcohols were prepared from the ketones with the aid of zinc and allyl iodide, the product of the reaction was decomposed with water and, in order to avoid stereochemical transpositions, driven over with steam, without adding any sulphuric acid.

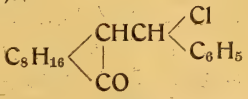
Zajcev looks upon the results of his investigations as a confirmation of Beckmann's opinion that *d*- and *l*-menthones are not mirror-images.

Wallach[1]) obtained many years ago, on condensing menthone with benzaldehyde in the presence of hydrochloric acid, a benzylidenementhone hydrochloride, to which Martine[2]) assigned the formula I. E. Boedtker[3]) tried to determine the constitution of this body by adding 5 g. of aluminium chloride to a solution of 25 g. of benzylidenementhone hydrochloride in 500 g. of benzene. After some days, when the evolution of hydrogen chloride had ceased, the mixture was poured into water, then dried and the benzene distilled off. As chief product, a body melting at 159° was obtained, which proved to be identical with a diphenylmenthylmethane, obtained by Boedtker through the action of magnesium phenyl bromide on benzylidenementhone[4]). As by-products, benzylidenementhone and a stereoisomeric diphenylmenthylmethane (m. p. 135 to 136°) had formed. As in Friedel-Craft's reaction chlorine is replaced by the phenyl group, Wallach and Martine's benzylidenementhone hydrochloride must have the structure of a menthophenylchloromethane, as expressed by formula II.

On condensing menthone with benzaldehyde in the presence of hydrochloric acid, Martine had obtained as by-product a chlorinated oil, which Boedtker investigated more closely and recognized to be a mixture of stereoisomeric menthophenylchloromethanes. It was impossible to induce it to crystallize. By heating with alcoholic potash lye under a reflux condenser, the mixture is converted into a new isomeric benzylidenementhone (α-benzylidenementhone). It is a yellow oil, boiling at 189° (12 mm.). On being oxidized with potassium permanganate in acetone, it yields as principal products benzoic acid, α,α'-methyl*iso*propyladipic acid and α-*iso*propylglutaric acid. When boiled with concentrated alcoholic potash lye, it forms menthone, benzoic acid and benzyl alcohol. The reaction with magnesium phenyl bromide leads to an isomeric diphenylmenthylmethane (m. p. 156 to 157°).



(I) Benzylidenementhone hydrochloride according to Martine.



(II) Menthophenylchloromethane.

Camphor. On page 63 of our October *Report* **1915**, we discussed a publication by H. Rupe[5]) concerning the influence of constitution on the rotatory power of optically active substances. Experimental details regarding the preparation of derivatives of methylenecamphor have now been described elsewhere by Rupe together with M. Iselin[6]).

Owing to the presence of the conjugation of the ethylenic and ketonic linkings in the derivatives of methylenecamphor of the type $C_8H_{14}\begin{cases}C:CH\cdot R\\ \dot{C}O\end{cases}$, these substances supply attractive material for such investigations.

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[1]) *Liebigs Annalen* **305** (1899), 261; *Report* October **1899**, 64. — [2]) Contribution à l'étude des menthones (Thèse, Paris 1904, page 66). — [3]) *Bull. Soc. chim.* IV. **17** (1915), 374. — [4]) *Compt. rend.* **145** (1907), 329; *Report* October **1907**, 160. — [5]) *Liebigs Annalen* **409** (1915), 327. — [6]) *Berl. Berichte* **49** (1916), 25.

The alkyl derivatives of methylenecamphor known so far were obtained by brominating the alkyl compounds, obtained through the action of alkyl haloids on sodiumcamphor, and transforming them into derivatives of methylenecamphor by splitting off hydrobromic acid. However, as Rupe shows, optically pure bodies do not always form. The methyl derivative, *e. g.*, prepared by Rupe and Iselin according to the method described hereafter, had a considerably higher optical rotation than the product described by Minguin and Haller[1]), in contrast to which it was solid too. The possibility of isomerism is, however, not excluded.

A process permitting of introducing any aliphatic or aromatic groups into methylenecamphor consists in the action of magnesium alkyl or aryl haloids on chloromethylene camphor. The latter can conveniently be prepared from hydroxymethylenecamphor and thionyl chloride.

$$C_8H_{14}\begin{cases}C{:}CH\cdot Cl\\ \dot{C}{:}O\end{cases} + MgRX = C_8H_{14}\begin{cases}C{:}CH\cdot R\\ \dot{C}{:}O\end{cases} + MgXCl.$$

The transposition, generally only a by-reaction with halogenated ketones, becomes here the chief reaction. The authors thus prepared methyl-, ethyl-, propyl-, *iso*butyl-, phenyl-, benzyl-, phenylethyl-, phenylpropyl-, *cyclo*hexyl- and α-naphthylmethylenecamphor.

The following facts are looked upon by the authors as proofs of that these bodies have the constitution of derivatives of methylenecamphor: — The compounds prepared with magnesium phenyl and *cyclo*hexyl bromides are perfectly identical with the benzylidene- and hexahydrobenzylidenecamphors obtained before in another way. An aliphatic and an aromatic derivative, on being split up by means of ozone, yielded camphoric acid and ample quantities of the camphorquinone to be expected according to the suggested formula. In one case, the other component (*iso*valeric acid) was easily detected, whereas phenylacetic acid, which ought to have formed on ozonation of the benzyl derivative, was present only in an extremely small quantity, because under the conditions chosen by the authors it was almost completely burnt by the ozone.

On refractrometric investigation of the liquid substances of the methylenecamphor group, a fairly considerable difference resulted, it is true, in the molecular exaltations of the aliphatic and aromatic compounds, but on the other hand the specific exaltations of both groups showed a remarkable conformity. The disturbance of the conjugation of the methylenic and ketonic double-linkings is caused by the camphor nucleus itself.

In order to prepare chloromethylenecamphor, $C_8H_{14}\begin{cases}C{:}CH\cdot Cl\\ \dot{C}O\end{cases}$, 1 molecule of dry hydroxymethylenecamphor is gradually introduced into 2 molecules of thionyl chloride. After some hours, the mixture is heated for half an hour on a water-bath up to 40°, and then the excess of thionyl chloride is distilled off at 50°. Chloromethylenecamphor boils at 113° (12.5 mm.); it is a colourless oil which, however, soon turns yellow, of strong, characteristic smell, recalling that of *Asarum europœum;* the reaction is endothermic to the extent of — 118 cal. for the formation of 5.22 g. of the chloro-compound.

In order to prepare methylmethylenecamphor (ethylidenecamphor), $C_8H_{14}\begin{cases}C{:}CH\cdot CH_3\\ \dot{C}O\end{cases}$, one proceeds as follows: into a flask containing 32.4 g. of magnesium shavings and 550 cc. of ether, and after the magnesium has been activated with a few drops of methyl iodide, a current of dry methyl bromide is passed for 16 hours under constant cooling and stirring. Having allowed the mixture to stand over night, one adds the magnesium methyl bromide solution drop after drop and under continual vigorous

[1]) *Compt. rend.* **138** (1904), 578.

stirring to 200 g. of chloromethylenecamphor, diluted with 200 g. of dry ether. In the beginning, a yellow salt forms as intermediate product, but in the course of the reaction a dark red liquid results which, on standing, separates into two unequal layers. After all the magnesium methyl bromide has been added, the mixture is allowed to stand for an hour and then decomposed by means of icy cold solution of ammonium chloride. In order to eliminate completely the halogenous bodies, the rectified product is boiled for 4 hours with 1 vol. of ethyl alcohol and 1 vol. of methyl alcoholic potash. Methylmethylenecamphor free from halogens melts between 28 and 29°; b. p. 109 to 110° (12 mm.); $[\alpha]_D + 178.58°$ (solution of about 10 per cent. in benzene). The smell is aromatic, camphor-like. Some crystalline bodies, melting between 280 and 281°, and 183 and 184°, had formed as by-products. Methylmethylenecamphor cannot be purified through distillation over sodium, as it then decomposes, forming camphor and a body melting between 169 and 170°.

The synthesis of ethylmethylenecamphor (propylidenecamphor), $C_8H_{14}\begin{cases}C:CH\cdot CH_2\cdot CH_3\\ CO\end{cases}$, is carried out like that of the methyl derivative just described, by the action of magnesium ethyl bromide on chloromethylenecamphor. It forms a colourless, aromatic oil, boiling between 121 and 122° (13 mm.); $d_{4°}^{20°}$ 0.9448; $[\alpha]_{D20°} + 172.95°$ (in alcoholic solution of about 10 per cent. + 171.26°; in a benzene solution of about 10 per cent. + 157.44°); n_D 1.49042. The purification of the crude product, containing chlorine, with the aid of alcoholic potash proved to be accompanied by a considerable loss; an attempt to eliminate the chlorinated products by treatment with aluminium amalgam led again to the substance melting between 169 and 170°.

n-Propylmethylenecamphor (*n*-butylidenecamphor), $C_8H_{14}\begin{cases}C:CH\cdot CH_2\cdot CH_2\cdot CH_3\\ CO\end{cases}$, boils between 131 and 132° (12 mm.); $d_{4°}^{20°}$ 0.9380; $\alpha_{D20°} + 161.95°$; n_D 1.48946. The product had been obtained free from chlorine by boiling with alcoholic potash and distilling over metallic sodium.

*Iso*butylmethylenecamphor (*Iso*amylidenecamphor), $C_8H_{14}\begin{cases}C:CH\cdot CH_2\cdot CH(CH_3)_2\\ CO\end{cases}$, may be freed from chlorine by boiling with alcoholic potash and distilling over sodium. B. p. 136 to 138° (12 mm.); $d_{4°}^{20°}$ 0.9275; $[\alpha]_{D20°} + 156.69°$; n_D 1.48772. It forms a rather liquid, aromatic oil. It yielded on ozonization camphorquinone (m. p. 198°), camphoric acid (m. p. 186 to 187°) and *iso*valeric acid (b. p. 173 to 174°).

The action of magnesium allyl bromide on chloromethylenecamphor did not lead to the expected camphor derivative, but to a mixture of hydrocarbons. On the contrary, from magnesium phenyl bromide and chloromethylenecamphor, phenylmethylenecamphor[1]) (benzylidenecamphor), $C_8H_{14}\begin{cases}C:CH\cdot C_6H_5\\ CO\end{cases}$, was obtained in the usual way. M. p. 98.5°; $[\alpha]_{D20°} + 426.55°$ (solution of about 10 per cent. in benzene).

Benzylmethylenecamphor (phenylethylidenecamphor), $C_8H_{14}\begin{cases}C:CH\cdot CH_2\cdot C_6H_5\\ CO\end{cases}$, boils between 124 and 126° (0.1 mm.); $d_{4°}^{20°}$ 1.0250; $[\alpha]_{D20°} + 129°$; n_D 1.54948. It was accompanied by a body boiling between 143 and 144.5° (14 mm.), presumably of the formula $C_{12}H_{14}O$. When submitted to ozonization, benzylmethylenecamphor gave

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[1]) This compound has been previously described by Haller and March. *Compt. rend.* **142** (1906), 316; *Report* April **1906**, 101.

camphorquinone, benzoic and camphoric acids with a little phenylacetic acid, the small yield of the last being due to the destructive action of ozone on this acid, with formation of formic acid.

From magnesium phenylethyl bromide and chloromethylenecamphor, phenylethylmethylenecamphor (phenylpropylidenecamphor), $C_8H_{14}\langle_{CO}^{C:CH\cdot CH_2\cdot CH_2\cdot C_6H_5}$, results. B. p. 152 to 154° (0.1 mm.); 208 to 210° (13.5 mm.); $d_{40}^{20°}$ 1.0094; $[\alpha]_{D20°}$ +127.99°; n_D 1.54035.

Phenylpropylmethylenecamphor (phenylbutylidenecamphor), $C_8H_{14}\langle_{CO}^{C:CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot C_6H_5}$, from phenylpropylmagnesium bromide and chloromethylenecamphor, boils between 221 and 223° (15 mm.); $d_{40}^{20°}$ 0.9990; $[\alpha]_{D20°}$ + 113.33°; n_D 1.53735.

*Cyclo*hexylmethylenecamphor (hexahydrobenzylidenecamphor), $C_8H_{14}\langle_{CO}^{C:CH\cdot C_6H_{11}}$, from magnesium *cyclo*hexyl bromide and chloromethylenecamphor, crystallizes in beautiful, colourless prisms; m. p. 46 to 48°; $[\alpha]_{D20°}$ + 128.13° (solution of about 10 per cent. in benzene)[1]).

α-Naphthylmethylenecamphor, $C_8H_{14}\langle_{CO}^{C:CH\cdot C_{10}H_7}$, is obtained through the action of magnesium α-naphthyl bromide on chloromethylenecamphor. M. p. 98 to 99.5°; b. p. 253 to 254° (12.5 mm.); $[\alpha]_{D20°}$ + 353.62° (solution of 10 per cent. in benzene).

Endeavours to prepare a diphenyl derivative of methylenecamphor remained unsuccessful, a mixture of diphenyl, benzerythrene and some bodies melting between 183 and 184°, 280 and 281°, and 138 to 143° being obtained. The compound of the last named m. p., which had formed but in a small quantity, is perhaps the diphenyl derivative looked for.

The action of magnesium, which had been activated as much as possible by means of iodine, on chloromethylenecamphor in a mixture of ether and benzene likewise led to the two substances, the m. p^s. of which lie between 183 to 184° and 280 to 281°.

The optical rotation of some of the methylenecamphor derivatives is lessened considerably on reduction. This is no proof, however, that a double linking considerably increases the optical activity, for it must be taken into account that a new asymmetric carbon atom forms: — $C_8H_{14}\langle_{CO}^{C:CH\cdot R} + H_2 = C_8H_{14}\langle_{CO}^{\overset{*}{C}H\cdot CH_2R}$.

Through the action of sodium amalgam on *iso*butylmethylenecamphor in methylalcoholic solution, *iso*amylcamphor, $C_8H_{14}\langle_{CO}^{CH\cdot CH_2\cdot CH_2\cdot CH(CH_3)_2}$, is formed. It is a colour- and odourless oil, b. p. 140° (14 mm.); $d_{40}^{20°}$ 0.9197; $[\alpha]_{D20°}$ + 66.78°; n_D 47015.

Benzylmethylenecamphor, on being reduced with sodium amalgam, is converted into phenylethylcamphor, $C_8H_{14}\langle_{CO}^{CH\cdot CH_2\cdot CH_2\cdot C_6H_5}$, m. p. 60 to 61°; b. p. 201 to 202° (15 mm.); $[\alpha]_{D20°}$ + 22.82° (solution of 10 per cent. in benzene).

In the same way, phenylethylmethylenecamphor yields phenylpropylcamphor, $C_8H_{14}\langle_{CO}^{CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot C_6H_5}$, b. p. 208 to 210° (15 mm.); $d_{40}^{24°}$ 1.0008; $[\alpha]_{D20°}$ + 52.37° (solution of about 10 per cent. in benzene); n_D 1.52883.

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[1]) See *Report* April **1906**, 101.

Fenchone. According to S. S. Nametkin and W. Chochrjakowa[1]), the hydroxyfenchone, obtained by Konowalow[2]) on reducing nitrofenchone, is in reality a diketone, $C_{10}H_{16}O_2$, for which they established two formulas. It is a heavy, colourless oil, which with time turns dark. B. p. 126.5 to 127° (11 mm.); $d_{4°}^{20°}$ 1.0028. It yields a disemicarbazone, decomposing at 200°, and a dioxime, m. p. 123 to 124°.

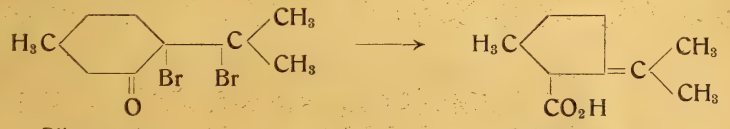
Carvone. When trying to condense acetone with carvone through heating with hydrochloric acid in a sealed tube, A. Müller[3]) observed the formation of carvacrol. This phenol was identified by its physical properties and the reaction with ferric chloride. The isomerization of carvone to carvacrol had been observed already under the influence of several reagents, but not with hydrochloric acid.

Müller further studied the isomerizations of carvomenthol, described by Kondakow and Lutschinin[4]). He prepared 8-chloro-Δ^6-terpene-2-one according to Goldschmidt and Kisser[5]); it cannot easily be purified, as it is very unstable. It yielded carvacrol on being heated, which yield may be increased considerably by altering the process.

Besides, Müller has been speculating on some of the intermediate products to which these isomerizations give rise, and has been able to confirm Kondakow's presumptions in many respects.

Pulegone. E. Sernagiotto[6]) has continued his studies of the autoxidations under the influence of light[7]) and examined the action of oxygen and water on pulegone, when exposed to sunlight. The same products are formed as through oxidation with potassium permanganate, *viz.*, acetone and β-methyladipic acid. Besides, an unsaturated ketolactone, $C_{10}H_{14}O_3$, is formed, m. p. 183.5°; its oxime melts at 116°. On oxidation with chromic acid mixture, the ketolactone yielded acetone and β-methylglutaric acid.

Many years ago, Wallach[8]) described the conversion of dibromopulegone into pulegenic acid under the influence of alkali as one of the most interesting transformations in the group of alicyclic compounds, such as realizes the change of one ring system into another.



Dibromopulegone. Pulegenic acid.

A fresh systematic and extensive investigation[9]) has now made it clear for him that the course of the interaction of dibrominated *cyclo*hexanones and alkali depends considerably on the position of the bromine atoms in the molecule and that, similar to what takes place when pulegenic acid is formed, almost any hexacyclic ketones may be converted into pentacyclic ketones, if one only starts from dibromoketones with adequate position of the bromine atoms and which it is an easy task to prepare. If two molecules of bromine are added to *cyclo*hexanone in glacial acetic acid, it seems that the bromine atoms distribute themselves in juxtaposition to a carbonyl

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[1]) *Journ. russ. phys. chem. Ges.* **47** (1915), 1611; *Chem. Zentralbl.* **1916**, II. 255. — [2]) See *Report* April **1904**, 113. — [3]) *Journ. f. prakt. Chem.* II. **93** (1916), 10. — [4]) *Ibidem* II. **60** (1899), 257. — [5]) *Berl. Berichte* **26** (1893), 488. — [6]) *Atti R. Accad. dei Lincei, Roma* (5), **24** (1915), 1065; *Chem. Zentralbl.* **1916**, I. 1147. — [7]) See *Report* October **1915**, 81. — [8]) *Liebigs Annalen* **289** (1896), 350; *Report* April **1896**, 44. — [9]) *Nachr. K. Ges. Wiss.* Göttingen **1915**, session on July 17th.

group each. Liquid dibromo*cyclo*hexanone forms on bromine being added to *cyclo*hexanone dissolved in glacial acetic acid. If the dibromide, after having been washed in order to free it from adherent acid, is shaken with aqueous potash lye, the reaction is completed after about an hour, a colourless solution having resulted. In the case of direct acidulation, only a very small quantity of an acid can be extracted from the liquid by means of ether. Steam, passed through the acid solution, carries with it a volatile compound which is coloured violet by ferric chloride, most probably the intermediate product $C_6H_8O_2$. With semicarbazide, it affords a very sparingly soluble compound, m. p. about 230°, which is perhaps an additive product of $C_6H_8O_2$ and semicarbazide.

If the filtered and alkaline original transposition product of bromo*cyclo*hexanone is evaporated with potassium hydroxide, the increasing concentration is accompanied by dark coloration. As soon as a brownish coloured substance begins to deposit on the walls of the vessel, one allows the mixture to cool, acidulates with sulphuric acid and extracts with ether. The α-hydroxycarboxylic acid, taken up by the ether, congeals to a crystalline mass on removal of the solvent. If the acid was sufficiently purified beforehand, it can be made colourless through distillation *in vacuo*. Recrystallized from water, it melted between 103 and 104°. It proved to be identical with an acid obtained according to Wislicenus by adding hydrocyanic acid to *cyclo*pentanone and decomposing the nitrile thus formed by means of hydrochloric acid. On heating the hydroxyacid from dibromo*cyclo*hexanone with peroxide of lead and dilute sulphuric acid, carbon dioxide was violently evolved and *cyclo*pentanone formed; dibenzylidene compound, m. p. 191°, semicarbazone, m. p. 209 to 210° (216 to 217° in case the heating is carried out rapidly).

All the reactions described run so smoothly and readily that the transformation of *cyclo*hexanone into *cyclo*pentanone may be shown as an experiment during a lecture.

The bromination of 1,2-methyl*cyclo*hexanone, dissolved in glacial acetic acid, with two molecules of bromine and under the previously mentioned conditions, takes likewise place smoothly and leads to a dibromide melting between 42 and 43°. The transposition of this dibromide with potash lye takes place easily. One succeeds in this case in seizing the first product of the reaction. If the alkaline solution is acidulated and distilled with steam, a snow-white, quickly congealing body passes over, $C_7H_{10}O_2$, m. p. 62 to 63°. It affords a violet-black colour with ferric chloride. The semicarbazone melts between 174 and 175°. The compound seems to be an unsaturated ketole.

If the body $C_7H_{10}O_2$ is heated with potash lye, an acid, $C_7H_{12}O_3$, is formed, m. p. 74 to 75°. When distilled, in aqueous solution, with lead peroxide and sulphuric acid, it splits off carbon dioxide and passes into 1,2-methyl*cyclo*pentanone; semicarbazone, m. p. 179 to 180°. It proved to be identical with a preparation from 1,2-methyl*cyclo*pentanone, derived from camphorphorone. This transformation of 1,2-methyl*cyclo*hexanone into 1,2-methyl*cyclo*pentanone may be looked upon as the best and most convenient method of preparing pentacyclic ketones.

The apparently self-evident supposition that the acid $C_7H_{12}O_3$ has to be considered as α-hydroxy*cyclo*methylpentanecarboxylic acid has, so far, not been confirmed by endeavours to build it up synthetically from 1,2-methyl*cyclo*pentanone hydrocyanide, for the substance thus obtained showed properties that differed somewhat from those of the acid described.

The conversion of 1,3-methyl*cyclo*hexanone into 1,3-methyl*cyclo*pentanone was carried out as well with active methyl*cyclo*hexanone from pulegone, as with the inactive ketone from *m*-cresol. The products obtained on bromination are liquid, the same as

the intermediate product (presumable formula: $C_7H_{10}O_2$) of the transposition of the bromide from 1,3-methyl*cyclo*hexanone and the hydroxyacid $C_7H_{12}O_3$ forming from it, either of which has not been investigated more closely as yet.

On being shaken with potash lye, the dibromide dissolves readily. After concentrating the alkaline solution, one obtains, on acidulation, an acid which, through distillation with lead peroxide and sulphuric acid, yields a ketone, fairly soluble in water. If active methyl*cyclo*hexanone from pulegone is used to start from, the 1,3-methyl-*cyclo*pentanone is dextrorotatory; dibenzylidene compound, m. p. 149 to 151°. The dibenzylidene compound of the inactive ketone melts between 155 and 156°.

Wallach then describes the transformation of 1,4-methyl*cyclo*hexanone into 1,3-methyl-*cyclo*pentanone. On brominating the former, a liquid dibromide was obtained, which readily dissolved when being shaken with potash lye. Neutral substances, which have not been investigated so far, formed as by-products, m. p^s. 201 to 203° and 149 to 157°, respectively. A liquid compound, colouring with ferric chloride, has not been observed. On boiling down the alkaline solution, an acid was obtained which could easily be isolated but proved not to be uniform. If heated with lead peroxide and sulphuric acid, it is converted into *i*-1,3-methyl*cyclo*pentanone; semicarbazone, m. p. 185 to 186°, dibenzylidene compound, m. p. 156 to 157°.

Dimethyl-1,3-*cyclo*hexanone-5 in glacial acetic acid yields on being brominated a mixture of two dibromides. The α-dibromide melts at 163 to 164°, the β-dibromide at 60 to 61°. The former is sparingly attacked by potash and is formed only in small quantity. On decomposing the β-dibromide with potash lye and distilling the liquid with steam, a readily congealing body, $C_8H_{12}O_2$, passes over, m. p. 71 to 72°. Its aqueous solution colours intensely dark with ferric chloride. It yields with boiling alkali an acid, $C_8H_{14}O_3$, m. p. 92 to 93°, which is converted into 1,3-dimethyl*cyclo*pentanone-4 by treatment with lead peroxide and sulphuric acid, when carbon dioxide is given off. Semicarbazone, m. p. 165 to 166°.

As primary material for the conversion of trimethyl-1,3,3-*cyclo*hexanone-5 (dihydro-*iso*phorone) into trimethyl-1,3,3-*cyclo*pentanone-5, *iso*phorone was used, which was reduced to dihydro*iso*phorone according to Skita's method. It easily affords a beautifully crystallizing dibromide, m. p. 90°. Potassium hydroxide converts it into a compound, $C_9H_{14}O_2$, readily volatile with steam, m. p. 89 to 90°, which colours violet black with ferric chloride and acts strongly reducing. On being heated with potash lye, it forms an acid, $C_9H_{16}O_3$, m. p. 88 to 89°, which is characterized by an almost insoluble ferric salt. Heating with lead peroxide and sulphuric acid leads to trimethyl*cyclo*pentanone, b. p. 159.5 to 161°; $d_{18°}$ 0.8785; n_D 1.4330; semicarbazone, m. p. 171 to 173.5°. The ketone has a penetrating smell of peppermint. On being oxidized with chromic acid, it yields a keto acid, $C_8H_{14}O_3$, with the same carbon content and the semicarbazone of which melts between 168 and 169°.

Menthone (methyl-1-*iso*propyl-4-*cyclo*hexanone-3) can be converted into dihydro-camphorphorone (methyl-1-*iso*propyl-3-*cyclo*pentanone-2). Bromination in glacial acetic acid leads to a dibromide, m. p. 79 to 80°, which according to Beckmann represents a 1,4-dibromomenthone. Wallach thinks it more probable that the bromine atoms are in 2,4-position. When the dibromide is shaken with potash lye, a mixture of products, $C_{10}H_{16}O_2$, forms, which is free from bromine and may be isolated by steam distillation of the mixture. The components (α- and β-) are separable through fractionated crystallization. The α-compound melts between 82 and 83°, b. p. 233 to 234°. The β-compound melts between 36 and 38° and seems to transform itself into the α-variety on keeping. Both compounds colour bluish black with ferric chloride. If heated

for some time with alkali, they are converted into methyl-1-*iso*propyl-3-α-hydroxy-*cyclo*pentane-2-carboxylic acid, $C_{10}H_{18}O_3$, m. p. 100 to 101°, which on oxidation yields dihydrocamphorphorone. The peroxide of lead and sulphuric acid method is not appropriate for its oxidation into the ketone $C_9H_{16}O$, as the acid is too sparingly soluble in water. The best method is to bind the acid to alkali, mix the aqueous solution of the salt with permanganate solution in excess, acidulate the mixture and distil with steam, when a ketone of menthone odour passes over under the formation of much foam. B. p. 184 to 185°; $d_{19°}$ 0.890; n_D 1.4410. We have here to deal with dihydrocamphorphorone (dihydropulegenone); semicarbazone, m. p. 198 to 199°.

When tetrahydrocarvone (carvomenthone) in glacial acetic acid is treated with bromine, a dibromide, $C_{10}H_{16}Br_2O$, is obtained which differs altogether from the isomerides arrived at on brominating dihydrocarvone direct, or dissolved in glacial acetic and hydrobromic acids. According to the active or inactive ketone used, active or inactive preparations are obtained. The new active dibromide from tetrahydrocarvone melts between 80 and 81°, the inactive variety between 66 and 67°. They are to be considered as dibromo-1,3-menthanone-2. With potash lye they yield the identical transposition products as dibromomenthone.

Through bromination of methyl-1-*iso*propyl-3-*cyclo*hexanone-5 (δ-menthone), a mixture was obtained, composed of an α-dibromide, m. p. 133 to 134°, and a β-dibromide, which has not been isolated as yet in a pure state. When the crude dibromide was shaken with potash lye, part of it dissolved, but a considerable part remained, mainly consisting of α-dibromide. Distillation of the filtered and acidulated liquid with steam led to a body $C_{10}H_{16}O_2$, m. p. 47 to 48°, which showed the characteristic coloration with ferric chloride. On extracting the acid liquid with ether, after the compound $C_{10}H_{16}O_2$ has been removed, an acid of the formula $C_{10}H_{18}O_4$ is obtained, m. p. 148 to 149°. It is presumably a dihydroxy acid. Quite another acid, $C_{10}H_{18}O_3$, forms when $C_{10}H_{16}O_2$ is heated with potash solution. On heating a solution of the resulting acid with peroxide of lead and sulphuric acid, it passes into methyl*iso*propyl*cyclo*pentanone; b. p. 191 to 192°; $d_{16°}$ 0.8881; n_D 1.4430. The semicarbazone melts between 150 and 151°, the oxime at 91 to 92°.

Phenols and phenol ethers.

Oxidation of phenols with unsaturated side chains by means of ozone. Regarding the methylhomovanillin, prepared some time ago by C. Harries and R. Haarmann[1]) through reducing methyleugenol ozonide, Harries and C. Adam[2]) now publish some details. It is a pale yellow, fairly thick liquid of a feeble, but agreeable, vanilla-like odour. B. p. 121° (0,35 mm.); $n_{D20°}$ 1.54257. The semicarbazone melts at 163°, not at 181°, as was formerly indicated. M. p. of the *p*-nitrophenylhydrazone, 159° (previous indication, 157°). The bisulphite compound of the methylhomovanillin is sparingly soluble.

When reducing the ozonide of safrole, homopiperonaldehyde (homopiperonal), a liquid body, was obtained. It has previously been prepared and described by Semmler and Bartelt[3]), who obtained it as a solid body, m. p. 69°, by oxidizing safrole with ozone in benzene solution. The constants established by Harries and Adam tally in no way with Semmler's. Refractive index (n_D 1.57117 according to Semmler, $n_{D20.5°}$ 1.55293

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[1]) *Berl. Berichte* **48** (1915), 32; *Report* April **1915**, 104. — [2]) *Berl. Berichte* **49** (1916), 1029. — [3]) *Berl. Berichte* **41** (1908), 2751; *Report* April **1909**, 130.

according to Harries and Adam) and density (d_{200} 1.295 according to S., $d_{20°}^{20°}$ 1.2626 according to H. and A.) differ considerably, the same as the b. p^s. (143 to 144° at 10 mm. according to S., 137° at 10 mm. according to H. and A.). The aldehyde obtained by Harries and Adam is a very liquid, almost colourless oil, which even after long standing does not show any inclination to crystallize. In their opinion, the solid aldehyde prepared by Semmler and Bartelt must be a polymeride, the more so as piperonal itself melts already at 37°. In order to prepare the homopiperonal, the safrole ozonide, which is insoluble in ether, was reduced in a mixture of 75 cc. of ethyl acetate and 75 cc. of ether.

Chavicol methyl ether can, by way of the ozonide, easily be converted into homoanisaldehyde, a colourless, highly refractive oil, b. p. 78 to 79° (1.4 to 1.5 mm.), which in dilution smells like heliotropin. $d_{4°}^{20°}$ 1.096; $n_{D20°}$ 1.53593. The semicarbazone melts between 175 and 176°, the phenylhydrazone at 95°.

It was in no way possible to obtain the corresponding aldehyde of myristicin by reduction of the ozonide. Apiole behaved in a similar way.

The phenols of Japanese lac. In a series of treatises by R. Majima, J. Nakamura and J. Kurosawa[1]) on the chief component of Japanese lac, we find described some reactions, the knowledge of which is interesting also for our special domain. In order to synthetize the *iso*hydrourushiol dimethylether[2]), Majima and Nakamura condensed methylvanillin with methyldodecyl ketone, dissolved in absolute alcohol, by adding a solution of sodium hydroxide. Crystals separated gradually and after a fortnight the reaction was completed under formation of a substance,

$$(CH_3O)_2^{3,4}C_6H_3 \cdot CH : CH \cdot CO \cdot (CH_2)_{11} \cdot CH_3,$$

m. p. 67 to 68°. On being reduced in ethereal solution with platinum black and hydrogen, the substance took up two atoms of hydrogen, forming the saturated ketone $(CH_3O)_2^{3,4}C_6H_3 \cdot (CH_2)_2 \cdot CO \cdot (CH_2)_{11} \cdot CH_3$, m. p. 61 to 62.5°. After having been heated for ten hours on a sand-bath with 15 times its weight of amalgamated zinc and hydrochloric acid, this saturated ketone was reduced to *iso*hydrourushiol dimethylether, m. p. 50 to 51°. It was identical with the compound obtained by condensation of veratrol with *n*-pentadecylic acid in the presence of aluminium chloride and by consecutive reduction. In order to prepare the *iso*hydrourushiol from the dimethylether it was heated with hydrobromic acid, when *iso*hydrourushiol resulted, m. p. 91°.

In a similar way, 3,4-dimethoxy-1-*n*-tetradecylbenzene was prepared from methylvanillin and methylundecyl ketone.

1-*n*-propyl-2,3-dihydroxybenzene, prepared by Kurosawa from *o*-eugenol, resembles the hydrourushiol in structure. Kurosawa reduced *o*-eugenol[3]) with platinum black and hydrogen to *o*-dihydroeugenol, which he demethylated by means of hydrobromic acid, when the 1-*n*-propyl-2,3-dihydroxybenzene formed, m. p. 70 to 72°. Through heating *o*-eugenol with sodium ethylate and dimethyl sulphate in alcoholic solution, Kurosawa obtained *o*-eugenol methyl ether, which he reduced with hydrogen and platinum black into 1-*n*-propyl-2,3-dimethoxybenzene. In a like manner, 1-*n*-propyl-3,4-dihydroxybenzene and 1-*n*-propyl-3,4-dimethoxybenzene (dihydromethyleugenol) were prepared from eugenol.

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[1]) *Berl. Berichte* **48** (1915), 1597, 1603. — [2]) Urushiol is the chief component of Japanese lac. Its structure has not been established completely so far. Hydrourushiol has been recognized by Majima (*Berl. Berichte* **48** [1915], 1593) to be 1-*n*-pentadecyl-2,3-dihydroxybenzene. *Iso*hydrourushiol distinguishes itself from hydrourushiol by the position of the pentadecyl group. It is a 1-*n*-pentadecyl-3,4-dihydroxybenzene. — [3]) See *Report* April **1914**, 144.

The occurrence of bergaptene in the fruits of common rue, and of xanthotoxin in the fruits of *Ruta chalepensis*, has been mentioned on p. 102 of this *Report*.

Pœonol. G. Péron[1]) has shown some years ago that pæonol does not occur free in the roots of *Pœonia Moutan*, Sims (N.O. *Ranunculaceæ*), but in the form of a glucoside. Since then Y. Asahina and G. Shirabe[2]) have synthetically prepared a glucoside of pæonol. They obtained from pæonol, with the aid of β-acetylbromoglucose, pæonyl-β-glucoside in the form of prismatic needles, m. p. 118°; α_D — 79°. It crystallizes with 2 molecules of water, which it loses at 59°, when the crystals turn opaque. It is readily hydrolyzed by mineral acids and by emulsin, so that it cannot be identical with the glucoside from the roots of *Pœonia Moutan*, which is not decomposed by emulsin. Tetra-acetylpæonyl-β-glucoside melts at 146°; $[\alpha]_D$ — 44.1°.

In a treatise, entitled "Contributions to the knowledge of phenol esters", J. A. Einhorn[3]) describes the constants of some phenol esters, which he prepared from the corresponding phenols and *iso*valeric acid in the presence of phosphoryl chloride; *viz.*, phenyl *iso*valerate (b. p. 225 to 250°), thymyl *iso*valerate, a colourless liquid of a smell like valerian and a taste reminding of thyme (b. p. 248 to 249° at 758 mm.; $d_{15°}$ 0.9590); *o*-cresyl *iso*valerate, a colourless, oily liquid of an agreeable, ethereal smell (b. p. 174 to 178° at 700 mm.; $d_{15°}$ 0.9894), *m*-cresyl *iso*valerate (b. p. 185° at 750 mm.; $d_{15°}$ 0.9895) and *p*-cresyl isovalerate (b. p. 176 to 178° at 758 mm.; $d_{15°}$ 0.9884).

Acids and lactones.

Camphenonic acid. On dry distillation of camphenic acid, O. Aschan[4]) obtained a mixture of two acids, one solid of the formula $C_9H_{13}O \cdot CO_2H$ (m. p. 134°), which he calls camphenonic acid; the other, unsaturated, liquid, monobasic, $C_8H_{13} \cdot CO_2H$, which he designates as camphenelauronolic acid. The former is highly stable when subjected to oxidizing influences: a boiling alkaline solution of permanganate did not act on it at all, whereas a mixture of concentrated and fuming nitric acids, on several days' boiling, sparingly evolved red fumes and attacked the acid but slowly. It is not oxidized either on three hours' boiling with chromic and acetic acids. This stability suggests that the keto group of the camphenonic acid is situated between two (tertiary) carbon atoms, which are not easily attacked.

Supposing that the camphenonic acid forms from camphenic acid by dehydration according to the formula hereafter, an easy explanation of the behaviour of the former is thus given. The fact that camphenonic acid is converted into camphenic acid by fusion with potassium hydroxide, or by heating in a solution of sodium in alcohol, is likewise a proof of above constitution. Camphenonic acid is the β-carboxylic acid of camphenilone. It distils undecomposed at from 310 to 312° under normal pressure. Such a stability of a β-keto acid is not known in either the aliphatic or the monocyclic series, but does not seem to be anything extraordinary with cyclic compounds, at least if the carboxyl is in certain positions. Camphenonic acid is converted by reduction into camphenolic acid, m. p. 99 to 100°. The preparation of the inactive camphenonic acid yields as by-product the active variety, $[\alpha]_D$ + 79.1° and — 79.2° (according to the

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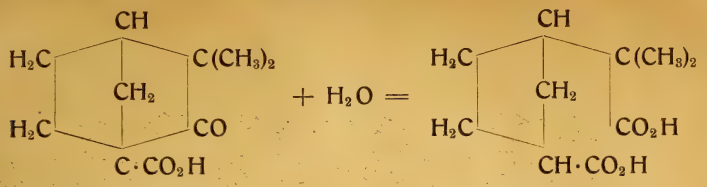
[1]) *Journ. de Pharm. et Chim.* VII. **3** (1911), 93, 238; *Report* April **1911**, 188. — [2]) *Journ. de Pharm. et Chim.* VII. **13** (1916), 222; *Journ. chem. Soc.* **110** (1916), I. 412. — [3]) *Bulet. Societ. de Stiinte din Bucuresti* **17** (1915), 51; *Chem. Zentralbl.* **1915**, II. 739. — [4]) *Liebigs Annalen* **410** (1915), 240.

rotation of the camphene used to start from). The optically active acid crystallizes with 1 molecule of water and melts at 70°; the anhydrous acid, between 105 and 106°. The inactive acid crystallizes without water.



Camphenonic acid. Camphenic acid.

Cinnamic acid. We pointed out on page 81 of our April *Report* **1915** that, according to E. Erlenmeyer, it was possible to obtain cinnamic acid and benzaldehyde in an optically active state by so-called asymmetric induction. E. Wedekind[1]) questioned at the time Erlenmeyer's indications regarding the optically active benzaldehyde and tried to explain the activation by the formation of an optically active compound of tartaric acid and benzaldehyde. Erlenmeyer[2]) meanwhile verified his investigations of the active cinnamic acids. He discusses at first the contiguous objection that the activity of cinnamic acid, as established before, might have been foreshadowed by the admixture of other optically active bodies. These, however, would have to be of an enormous rotatory power, unattained by far up to now, to be able to afford the high rotatory values observed, without sensibly interfering with the uniformity of the cinnamic acid. It was further investigated up to what limit the admixtures of tartaric acid and cinnamate in the preparation could be ascertained, the analytical carbon value being found to be the most sensitive indicator. From preparations, in which a content of from 2 to 10 per cent. of cinnamate was to be presumed according to this method, it was possible to remove it through recrystallization from ligroin. The cinnamic acid thus purified remained strongly active. In preparations, showing a difference of only 0.05 to 0.06 per cent. in the carbon content, the main part of the rotation must in any case be ascribed to the active cinnamic acid, and to it alone if the differences are still smaller.

Interesting particulars about the properties of allyl and methyl cinnamates, polymerized in direct sunlight, have been published by C. Liebermann, G. Mühle and M. Kardos[3]). The former can conveniently be purified by shaking it with methyl alcohol, which must be continued until a sample of the alcohol used for washing evaporates without leaving any residue. The purified ester forms a white, loose powder, which readily dissolves in chloroform. Cold benzene makes it gelatinize, but a good solution is obtained on heating. It was impossible to saponify the ester through boiling it for a considerable time with a 20 per cent. alcoholic potash lye. After having been dried at 110°, about 25 per cent. of the ester had become completely insoluble in chloroform. If the temperature is raised, this change takes place to a greater extent. The optimum of the converting temperature lies between 138 and 140°.

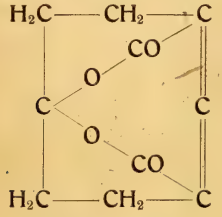
The methyl cinnamate polymerized by light dissolves well in chloroform. Light petroleum precipitates it from concentrated solutions as a fine, white powder, melting a little above 300°. On being heated up to 140° for some time, methyl polycinnamate

[1]) *Berl. Berichte* **47** (1914), 3172. — [2]) *Biochem. Zeitschr.* **74** (1916), 137; *Chem. Zentralbl.* **1916**, II. 57 — [3]) *Berl. Berichte* **48** (1915), 1645. Comp. C. Liebermann and M. Zsuffa, *ibidem* **44** (1911), 845; C. Liebermann and M. Kardos, *ibidem* **46** (1913), 1065.

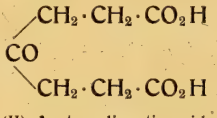
likewise becomes insoluble in chloroform. The light-polymerized benzyl and octyl cinnamates remain soluble in cold chloroform, even after having been heated for a long time up to 140°.

Constitution of anemonin. On page 80 of our April *Report* 1915, we have discussed a treatise by Y. Asahina on anemonin (I), the volatile component of some anemones. The author thinks to have proved the presence of two double linkings in the molecule of this interesting body. In the meantime, he has issued another publication on the constitution of anemonin[1]), in which is shown that it must be considered as a lactone. On heating it with alkali on a water-bath, an alkaline solution is obtained, provided the quantity of alkali exceeds what is necessary in order to neutralize two carboxyl groups. Ammoniacal solution of silver and Fehling's solution are reduced by anemonin in the heat. It forms a condensation product with phenylhydrazin, which indicates the presence of a carboxyl group. No semicarbazone or oxime could be obtained. Asahina identified the acetonediacetic acid (II) (hydrochelidonic acid) as an oxidation product of the potash salt of anemonic acid. He looks upon anemonin as a dilactone of a *cyclo*octanonedienedicarboxylic acid. On saponification of the lactone group, two keto acids, anemonic and anemoninic acids (III), are obtained.

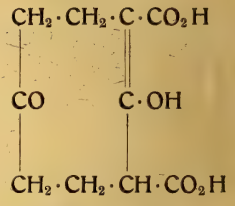
The results of later investigations of the anemonin have been published by Asahina[2]) elsewhere. He repeated Beckurts'[3]) bromination experiments and was able to confirm his indications, with the exception that he found the m. p. of tetrabromoanemonin at



(I) Anemonin.



(II) Acetonediacetic acid.



(III) Anemoninic acid.

175°, whereas Beckurts mentions 205°. It is remarkable that anemonin absorbs the bromine rather sluggishly. Not only with bromine, but also with hydrogen halogenides, anemonin behaves like a doubly unsaturated body, forming with hydrobromic acid a beautifully crystallizing dihydrobromide, m. p. 182°.

The so-called anemoninic acid (III), which forms on hydrolysis of anemonin with absorption of two molecules of water, had been obtained before only in the amorphous state and analyzed as salt. Asahina has now prepared it in the form of white, needle-shaped crystals, m. p. 116 to 117°. Beckurts indicates the same m. p. for the amorphous product. Asahina does not share Beckurts' view that the anemoninic acid is a hydrate of the anemonic acid, but thinks that relation far more complicated. The colour reaction with alkali, not shown by anemonic acid, is a characteristic of anemoninic acid. If anemonin is heated with an exactly equivalent quantity of alkali hydroxide solution, a passing reddish-brown coloration is noticed, which disappears quickly as soon as the hydrolysis is completed, leaving the solution pale yellow. The neutral alkali anemoninate is but slightly yellow, the reddish-brown colour reappears, however, on addition of a few drops of alkali. This behaviour may best be explained by the

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[1]) On the constitution of anemonin. Yakugakuzasshi, 1915, February number, page 1; *Journ de Pharm. et Chim.* VII. **12** (1915), 293. — [2]) *Arch. der Pharm.* **253** (1915), 590. — [3]) *Ibidem* **230** (1892), 205.

presence of at least one mobile hydrogen atom in the anemoninic acid, which is substituted by the alkali with formation of a coloured ion. Similar instances are known already. Anemoninic acid has perhaps the structure expressed by formula III. On catalytical reduction, it absorbs only one molecule of hydrogen, forming anemonolic acid, whereas anemonic acid takes up two molecules of hydrogen without any difficulty. This likewise proves that the structure of anemoninic acid differs entirely from that of anemonic acid.

Beckurts converted anemonin into anemonic acid, $C_{10}H_{10}O_5$, through boiling with water and oxide of lead. H. Meyer[1]) obtained the same acid later on from dimethyl-anemonin by hydrolysis with dilute hydrochloric acid. Anemonic acid melts at 210°. On saponification of anemonin with alkali alcoholates, dissolved in absolute alcohol, Asahina obtained alkali salts, the composition of which corresponded fairly well with that of alkali anemonate. If treated with acetate of lead, they yield a lead salt, from which an acid can be isolated showing the composition of anemonic acid. It does not melt at 210°, however, but at 120° and can be converted into an acid melting at 210° by boiling with dilute hydrochloric acid. The author calls the former α-anemonic acid, the latter β-anemonic acid. α-Anemonic acid forms a semicarbazone melting at 220° and a phenylhydrazone melting at 235°; β-anemonic acid, a semicarbazone melting at 270° and a phenylhydrazone melting at 240°.

Anemolic acid, $C_{10}H_{14}O_6$, was first prepared by Meyer by reducing anemonin with zinc and alcoholic hydrochloric acid. Asahina found that the same acid forms on catalytic reduction of anemoninic acid. It melts at 65° and yields with semicarbazide a sparingly soluble compound, the constitution of which has not been ascertained so far.

Nitrogenous bodies.

Indole and skatole. E. O. von Lippmann[2]) calls attention to the occurrence of indole and skatole when extracting sugar from molasses by the strontia method. Everybody, who has once entered a room where sugar is extracted by means of strontia or baryta, will remember the nauseous, sometimes almost unbearable fæcal smell of the vapours, evolved by the molasses on continued boiling with the alkaline earths. It is still more pronounced in certain condensates of such vapours, prepared sometimes for the purpose of turning to advantage their comparatively high content of ammonia. Indole and skatole were ascertained to be the cause of this smell. The indole showed the known colour reaction and melted at 52°, skatole at 95°. Both yielded a picrate and were successfully analyzed. von Lippmann supposes that the residues of albumines and their resolution products are responsible for the yield of indole and skatole.

[1]) *Monatsh. f. Chem.* **17** (1896), 297; **20** (1899), 635. — [2]) *Berl. Berichte* **49** (1916), 106.

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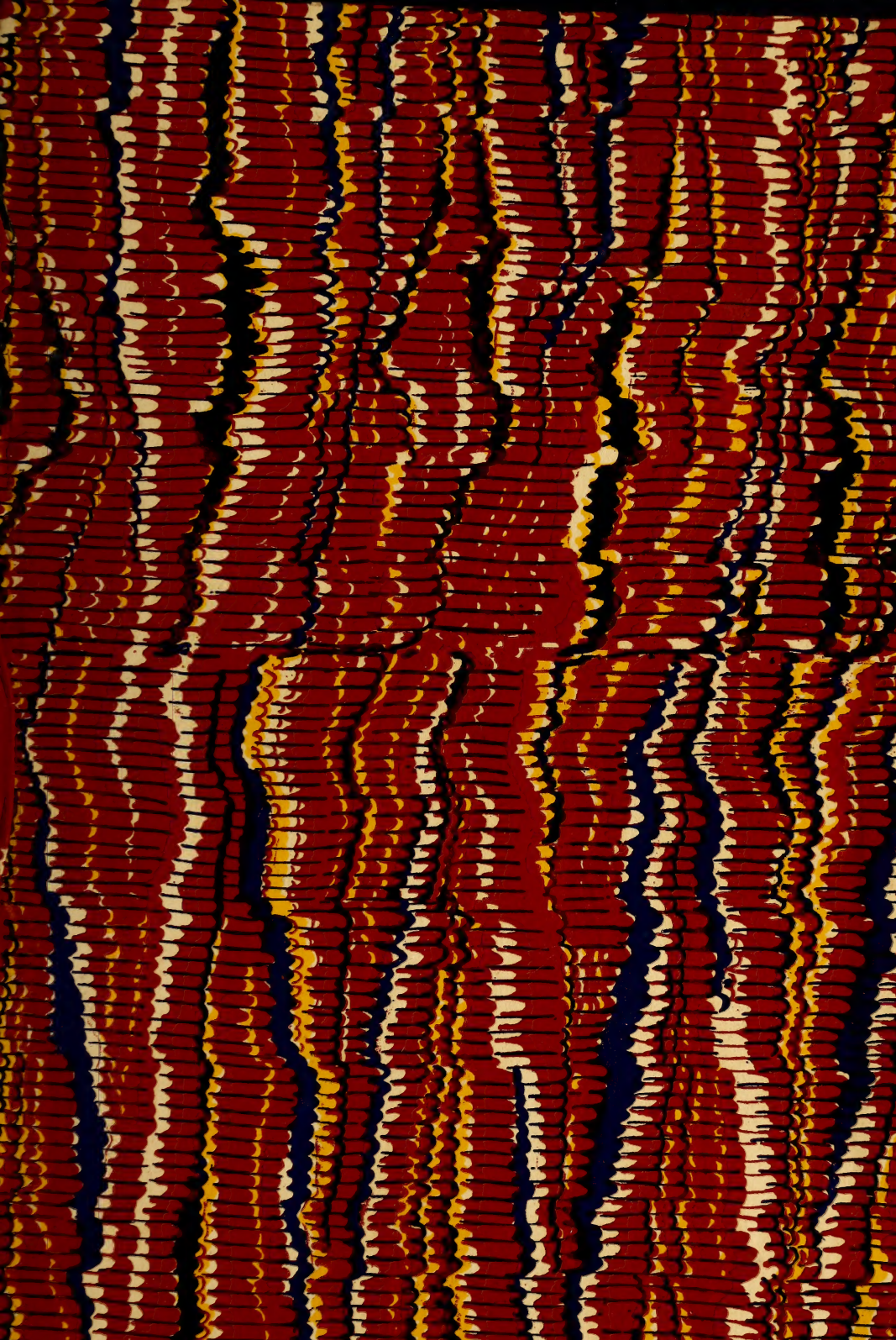

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